UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 5
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CHICAGO, IL 60604-3590

REPLY TO THE ATTENTION OF

WC-15J

MEMORANDUM

DATE: November 5, 2018

SUBJECT: EPA Northeast Juneau County Groundwater Investigation Data Analysis - Relationships between Nitrate in Groundwater and Potential Sources

FROM: Dean Maraldo, Environmental Scientist
Water Enforcement and Compliance Assurance Branch

TO: Ryan Bahr, Chief, Water Enforcement and Compliance Assurance Branch, Section 2

Patrick F. Kuefler, Chief, Water Enforcement and Compliance Assurance Branch

CC: [redacted], Associate Regional Counsel
Office of Regional Counsel

I. INTRODUCTION

This memo presents data analysis based on the results of an investigation summarized in EPA's August 30, 2018, Northeast Juneau County Groundwater Investigation *Sampling Inspection Report* ("Inspection Report") (EPA, 2018). The Inspection Report provided a description of EPA investigations related to potential sources of nitrate contamination in groundwater in northeast Juneau County, Wisconsin. The study area encompasses approximately 30 square miles, mostly within the Town of Armenia. The Inspection Report also included the results of the various sampling and inspection efforts, including the groundwater study conducted by EPA in northeast Juneau County during the week of April 30, 2018. This memo summarizes EPA's evaluation of the groundwater data collected as part of the groundwater study.

The groundwater study effort was in response to citizen complaints regarding concerns about elevated levels of nitrates in residential wells in northeast Juneau County. The purpose of the groundwater study was to investigate potential sources of nitrate contamination in the groundwater and in residential drinking water wells. The study focused on potential nitrates sources including crop fields, Central Sands Dairy (CSD), a large concentrated animal feeding operation, residential septic systems, and cranberry fields. EPA relied on a combination of standard analytical methods and research methods to meet the data collection and analysis goals of the groundwater study. The details regarding EPA's sampling design for the groundwater study are included in the Inspection Report.

The importance of EPA's efforts in this area was reinforced by the results of a residential well sampling study conducted in May 2018 by the Juneau and Wood County Health Departments and Land and Water Resource Departments, in conjunction with the University of Wisconsin-Stevens Point. The counties sampled 104 residential wells as part of the survey and reported that 41% of the wells tested had nitrate levels exceeding the drinking water standard of 10 mg/l. The counties issued a press release on June 15, 2018, providing a summary of the survey results and warning residents of risks related to nitrates (Juneau and Wood County Health Department, 2018). The press release also mentioned that the "percent of wells observed with high nitrate levels, through this survey, is greater than the estimated statewide average of 9% of wells."

II. STUDY SCOPE

As discussed above, the purpose of the groundwater study was to investigate potential sources of nitrate contamination in the groundwater and in residential drinking water wells in the Town of Armenia, Wisconsin. EPA Region 7 assisted with the investigation by providing a direct-push boring technology hydraulic sampling machine, called a Geoprobe®, and two trained operators. Each groundwater sample collected with the Geoprobe® was located within a road right-of-way. The field investigation portion of the study began on April 30, 2018, and consisted of the following:

- Collection of groundwater samples (at two depths) from 41 temporary boring locations installed with a Geoprobe®. A total of 82 samples were collected for laboratory analysis.
- Pre-screening of the groundwater samples using Hach Nitrate Test strips, and a Fisher Scientific Accumet Waterproof Hand-held meter (A-85) for pH/ temperature.

EPA Region 5 scientists mapped five transects in the study area, identified as A through E. Transect A was designed to characterize the groundwater upgradient of crop fields and downgradient of cranberry fields and other potential sources upgradient of the CSD facility and nearby crop fields. The remaining transects (B-E) were designed to characterize groundwater both downgradient and upgradient of potential sources including, the CSD facility, crop fields, and cranberry fields. The location of the study area, including the temporary groundwater sample locations, direction of regional groundwater flow, and potential nitrate sources such as crop fields, the CSD facility, and cranberry fields, is shown in Figure A-1 (Appendix A).

For each Geoprobe® location, groundwater grab samples were collected at two depth intervals (ranging from 20-34' and 36-49' below ground surface), via a dedicated tube inserted into the Geoprobe® casing and down to a four-foot long retractable screen at the bottom of the casing. Prior to sample collection, the Geoprobe® operators pumped approximately one gallon of water out through the tubing to reduce the turbidity in the samples collected. Samples were collected for field analysis, including pH and temperature, and for nitrate analysis using the Hach Nitrate test strips. Samples collected for nutrients (total phosphorus, ammonia-nitrogen, total kjeldahl nitrogen, nitrate-nitrite nitrogen, total organic carbon), total metals, anions (bromide, chloride, fluoride, nitrate, and sulfate), and total dissolved solids, were analyzed by the EPA Chicago

Regional Laboratory (CRL). EPA also collected samples for N15 isotope, O18 isotope, and nitrates and shipped the samples to the Nebraska Water Center at the Water Sciences Laboratory at the University of Nebraska Laboratory (UNL) for analysis. EPA completed groundwater sampling activities on May 3, 2018. The Inspection Report (Section 2.4), summarizes the data results, and discusses EPA's data usability review and validation effort.

The main potential sources of nitrogen from CSD include dairy waste lagoons; manure piles; and manure and synthetic fertilizers applied to crop fields. For crop fields, the main sources are synthetic fertilizers and manure applied to the land to improve plant growth. For septic systems, nitrogen from human waste can migrate from septic systems into the groundwater and nearby drinking water wells. For cranberry fields, a source of nitrogen is synthetic ammonia-based fertilizer (Bohlke, 2002). The forms of nitrogen discussed above typically migrate through the unsaturated sands in the area and enter the groundwater via preferential pathways. The nitrogen is converted to nitrate through chemical and biological processes. Groundwater contaminated with nitrate can be pumped up in drinking water wells.

Study Limitations

There are some limitations in the study to note. First, with the exception of five residential well samples, EPA collected water samples from temporary borings, as discussed above. Temporary borings are not as well developed as established drinking water wells, and often more turbid. To address this limitation, EPA relied on four types of nitrogen analysis methods for groundwater samples. EPA used nitrate colorimetric test strips (Hach® test strips) as a field screening tool to measure nitrate concentrations in increments of 0, 1, 2, 5, 10, 20, and 50 mg/l. EPA also had groundwater samples sent to UNL for nitrate+nitrite-nitrogen, Nitrogen N15 isotope, and Oxygen O18 isotope analyses. The isotope data is used to distinguish commercial fertilizers from organic sources (animal and/or human). Finally, groundwater samples were sent to CRL for nitrate-nitrite N analysis (ASTM D7781-14), and nitrate-N (EPA Method 300.0).

Field preservation of samples with high levels of sediment is known to be difficult and although samples may meet the pH target in the field, the preservative can continue to react with the sediment resulting in changes in the sample's pH when it arrives at the lab. After the shipment of the first round of samples, CRL notified the EPA Team that the nitrate-nitrite N analysis (ASTM D7781-14), samples were arriving at the laboratory under preserved (i.e., higher than a pH of 2). After receiving this notification, the EPA Team added preservative to the samples that were to be shipped to CRL Laboratory on May 3, 2018. This led to some of the samples being over-preserved. According to CRL, ". . . The over-preservation interferes with the analysis and the sample data may be estimated. This issue has been previously seen with nitrate-nitrite nitrogen results for other projects where samples were over-preserved . . ."

EPA conducted a quality assurance review of nitrate data received from UNL, CRL (nutrient and anion analysis), and Hach® Nitrate Test Strip for Nitrate. Table A-1 summarizes the four sets of nitrogen analysis. Through comparisons of the four data sets, EPA identified samples where the results from the CRL nitrate-nitrite nitrogen method were inconsistent with the results from the other three data sets. Eleven of the samples had results above 10 mg/L in three (UNL nitrate+nitrite-nitrogen, CRL nitrate-nitrogen via method 300.0 and Hach® Nitrate Test Strips) of the four data sets, including in one of the two CRL data sets. The other CRL data set (nitrate-nitrite N method ASTM D7781-14 in water) reported "U" for not detected for these eleven sample results. As part of this comparison to other data, EPA also evaluated the correlation between the four nitrogen data sets and found a strong correlation with the exception of the eleven samples with the inconsistencies noted above and sample A2a which is discussed further below. These eleven samples were all part of the same shipment shipped to CRL Laboratory on May 3, 2018. See Appendix A, Figures A-20 and A-21 for comparisons of CRL nitrate-nitrite N and CRL nitrate-N, and TDS and CRL nitrate-nitrite N, with and without inconsistent data.

EPA also further reviewed the five matrix samples spike results. Three of the matrix spike results had a pH of 2 and the other two had pH of 1. For two of the three matrix spikes with pH of 2, the spike recoveries were higher than the recovery range of 90-110%. This is indicative of positive interference and is discussed further after Table A-1. The other matrix spike with a pH of 2 was within the acceptable range. For one of the pH 1 samples, the spike recoveries were higher than the range and indicative of positive interference. The other sample with pH of 1, was reported as not detected when spiked with 2.0 mg/L of nitrate. It is expected that the method would detect some amount of nitrate when a sample is spiked with a known amount of nitrate. In this instance, the method failed to detect any of the nitrate, raising concern with the use of non-detect data at a pH of 1. The observed matrix interference may help explain the inconsistencies highlighted in pink in Table A-1, and may be related to over preservation.

Based on the feedback from CRL, the matrix spike data, and the comparison between the four nitrogen data sets, EPA did not map in Figures A-6 and A-7 the results for the any of the nitrate-nitrite N samples shipped to CRL on May 3, 2018.

EPA also did not map sample A2a which also was inconsistent with results from the other three data sets and had following quality assurance concerns:

- CRL's nitrate-nitrite N method ASTM D7781-14 in water result was 36.90 mg/L. The Hach® Nitrate Test Strip results, the UNL data and the CRL nitrate-nitrogen via method 300.0 data were all non-detect for forms of nitrogen.
- The April 30, 2018 nutrient sample bottles were in a cooler with total metals sample bottles. In order to properly preserve the total metals sample bottles, the total metals sample bottles were opened to add preservative. Based on the results for the A2a nutrient sample, there is a possibility that sample A2a was contaminated with the nitric acid preservative that was being used to preserve the total metals samples.

In this memo, designations of upgradient and downgradient are based on a regional groundwater flow study conducted by Lippelt (1981). EPA is not aware of any more recent regional groundwater flow studies.

EPA obtained copies of documents regarding CSD's nutrient management practices during a June 2017 inspection of the CSD facility, and from the Wisconsin Department of Natural Resources (WDNR). CSD's SnapPlus Spreading and Nutrient Management Crop Report, sorted for Crop Year 2015, provides product name and analysis for fertilizers used on the crop fields. The SnapPlus report provided application rates, methods and total amount of fertilizers applied. Inorganic fertilizer sources used by CSD include ammonium sulfate, aspire, potash, Cal-Sul, 32% UAN (Liquid 32-0-0), Corn Popper (different analysis), and Potato Starter. Organic sources include post digester solids and post digester liquids. However, the information does not include dates of application.

Finally, EPA has limited information about the crop fields in the study area that are not covered under CSD's Nutrient Management Plan.

III. NITROGEN IN THE ENVIRONMENT

Nitrogen comprises approximately 80 percent of the earth's atmosphere and is found in the environment in many forms including nitrate (NO_3-), and nitrite (NO_2-). Oxidized forms of nitrogen, such as nitrate, are soluble in water and can move through the soil system and make their way to groundwater, resulting in potential exposure of human to nitrates in drinking water. Nitrogen is transformed in the environment from one form to another through processes such as nitrogen fixation, mineralization, nitrification, and denitrification.

Nitrogen contamination in groundwater can be attributed to a number of sources, including fertilizers, animal wastes, and domestic wastes. Synthetic fertilizers are the largest sources of reactive nitrogen input to agricultural systems, followed by nitrogen fixation in cultivated croplands, atmospheric deposition, and manure production (EPA-SAB-11-013, 2011). While many fertilizers may be composed of nitrate, urea or ammonia are often used. The urea and ammonia are ultimately converted to nitrate by soil bacteria (EPA, 2013).

Nitrate is soluble in water and can easily pass through soil to the ground-water table, persisting in ground water for decades and accumulating to high levels as more nitrogen is applied to the land surface every year (Nolan, Hitt, & Ruddy, 2002). Well drained soils, such as the course-grained sands found in the study area, transmit water and nitrate rapidly to the groundwater table. In general, unconsolidated sand and gravel aquifers are porous and allow rapid movement of water, making them more susceptible to contamination from nitrate (USGS, 2005).

Nitrate in groundwater drinking water systems is of concern because private self-supplied drinking water systems are not federally regulated. Concentrations of nitrate greater than 3 mg/l generally indicate contamination (Madison and Brunett, 1985), and a more recent nationwide study found that concentrations of nitrate over 1 mg/l indicate human activity (Dubrovsky et al. 2010). EPA established a maximum contaminant level (MCL) for nitrate in drinking water of 10 mg/L under the Safe Drinking Water Act to protect against blue-baby syndrome in infants and susceptible individuals, which can lead to death in extreme cases (Ward 2005).

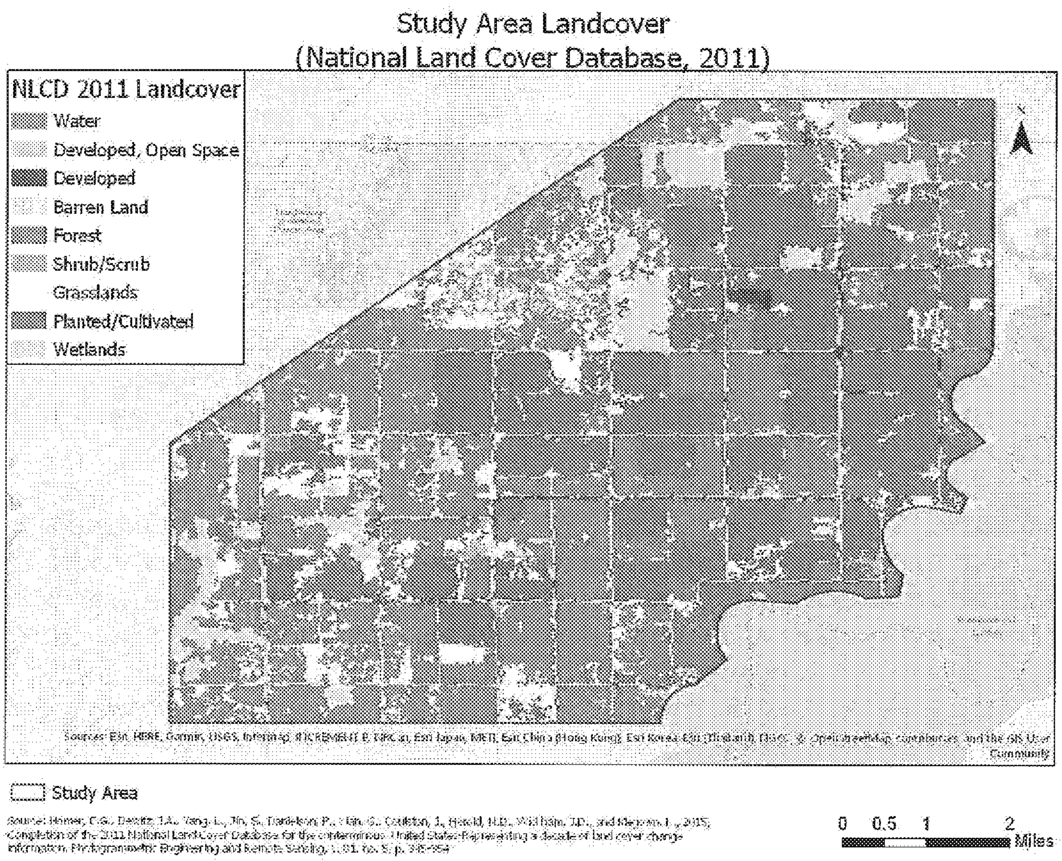
IV. STUDY AREA

The study area encompassed most of the Town of Armenia, a rural area with a population of approximately 699 people, and a population density of 8.99 people per square mile (U.S. Census Bureau, 2018). Based on the 2011 National Land Cover Database, land cover in the study area is dominated by forest, planted/cultivated, and grassland/herbaceous cover types, as summarized in Table 1 and Figure 1, below (Homer, et. al, 2015).

Table 1. Study area land cover (from Homer, et. al, 2015).

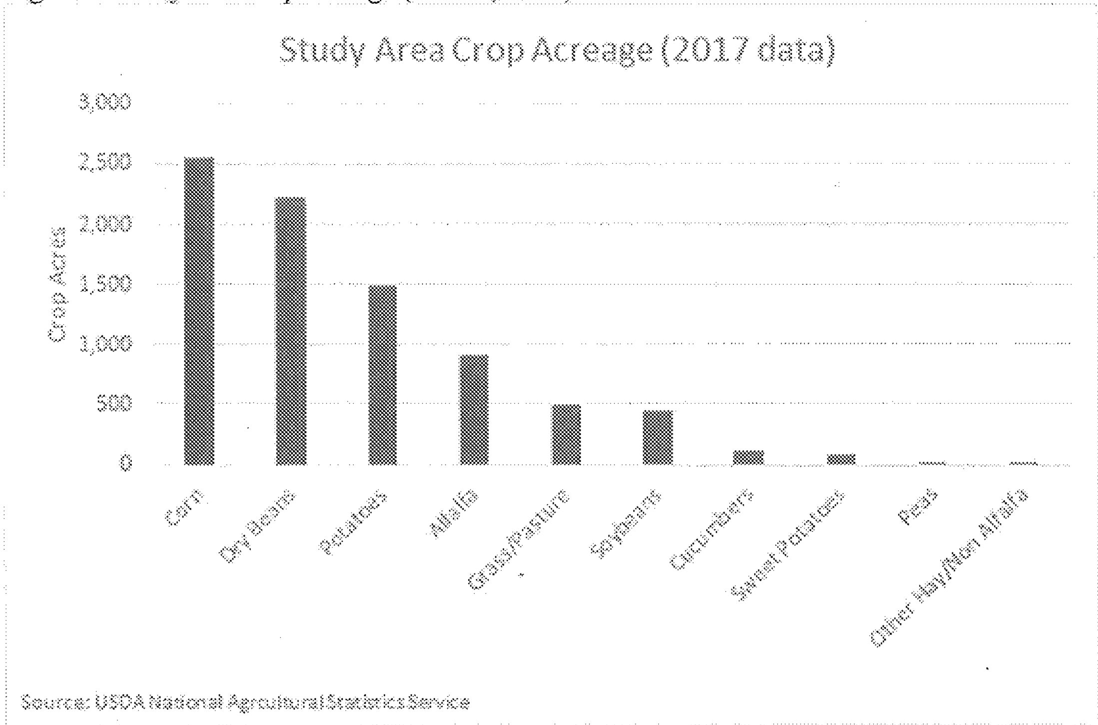
Land Cover Class	Area (acres)	Area %
Open Water	29	0.1%
Developed	1,441	5.8%
Barren Land	3	0.0%
Forest	10,436	41.9%
Shrub/Scrub	537	2.2%
Grassland/Herbaceous	3,068	12.3%
Planted/Cultivated	7,857	31.5%
Wetlands	1,538	6.2%
Totals	24,909	100.0%

Figure 1. Study area land cover.



Agricultural land use is dominated by cropland, and includes a concentrated animal feeding operation (CSD), and cranberry operations (Figure A-1). As summarized in Figure 2, corn, dry beans, and potatoes are the dominant crop type in the study area (USDA, 2018).

Figure 2. Study area crop acreage (USDA, 2018)



Geology

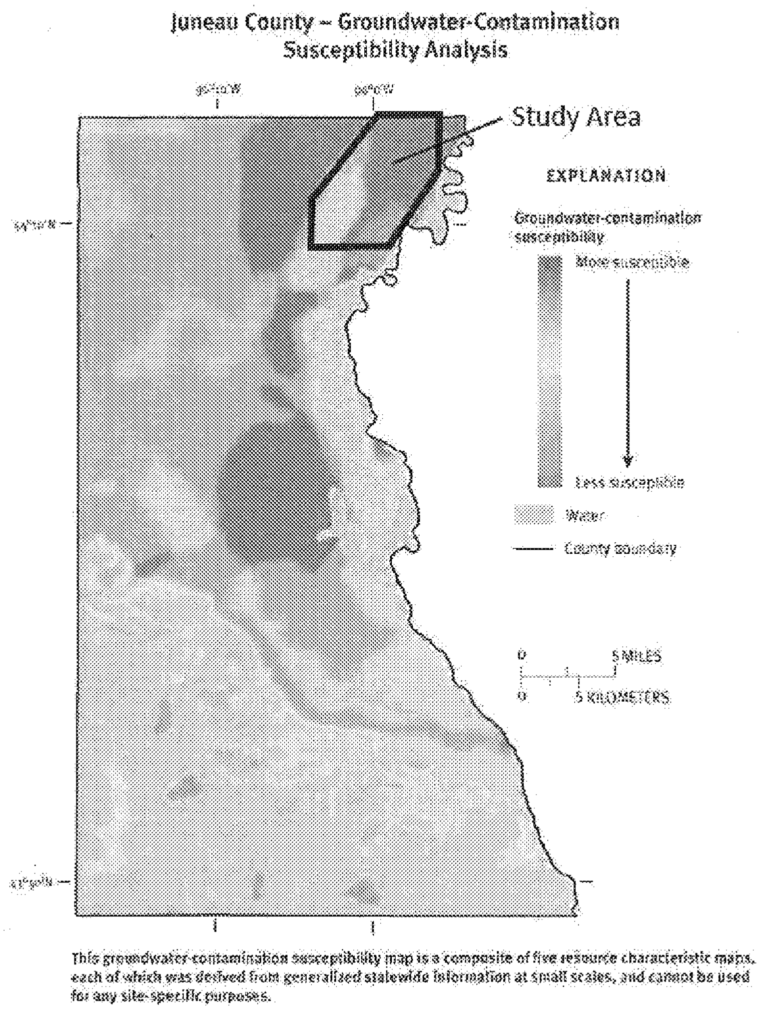
The study area encompasses approximately 30 square miles in northeast Juneau County, mostly within the Town of Armenia, Wisconsin. The study area also lies within the Central Sand Plain Region of Wisconsin, a relatively flat expanse of sand that covers over 3,000 square miles of Wisconsin. The sand originated as glacial outwash deposits into Glacial Lake Wisconsin, which came into existence about 19,000 years ago when the Green Bay Lobe of the Wisconsin glaciation blocked the ancient river that ran through the valley now occupied by the Wisconsin River (WDNR, 2015). The sand deposit exceeds 50 meters in depth in some areas of northeast Juneau County (Clayton, 1989). Bedrock in the area consists of Late Cambrian sandstone underlain by Precambrian igneous and metamorphic rock.

Groundwater – Surficial Sand Aquifer

The flow of groundwater in the surficial Central Sand Plain aquifer within the study area is generally in the southeasterly direction toward Lake Petenwell (Figure A-1). Residential drinking water well depths typically range from 20 to 65 feet in the study area, with some wells exceeding 120 feet in depth. High capacity wells are common in the area and provide water for industries and agriculture. Estimates of groundwater velocity in the Central Sand Plain aquifer range from approximately 0.5 to 1.0 feet per day to several feet per day (Lippelt and Hennings, 1981; Meigs & Bahr, 1993).

WDNR conducted a groundwater susceptibility analysis for Juneau County, in cooperation with the University of Wisconsin-Extension, Wisconsin Geological and Natural History Survey and the U.S. Geological Survey. The study identified portions of northeast Juneau County as areas "more susceptible" to groundwater contamination based on five physical resource characteristics, including depth to bedrock, type of bedrock, soil characteristics, depth to water table and characteristics of surficial deposits (see Figure 3; Schmidt, 1987).

Figure 3. Juneau County – Groundwater-Contamination Susceptibility Analysis (Schmidt, 1987), with study area overlay.



V. STUDY FINDINGS

As discussed above, the purpose of this study was to investigate potential sources of nitrate contamination in the groundwater and in residential drinking water wells in the Town of Armenia, Wisconsin. EPA evaluated the results of nitrogen samples, including isotope analysis, along with results of other parameters including anions (bromide, chloride, and sulfate), from groundwater samples collected via temporary borings. The study findings are summarized below, based on parameter and analytical technique.

Nitrogen

The results of the four nitrogen analyses conducted, including UNL nitrate+nitrite-N, CRL nitrate-nitrogen via method 300.0, CRL nitrate-nitrite N method ASTM D7781-14, and Hach® Nitrate Test Strips, are summarized in Table A-1. To support spatial analysis, the results of each of the four datasets were plotted on maps at two depth ranges (shallow and deep), along with potential sources, including crop fields, cranberry fields, and CSD (Appendix A, Figures A-2 through A-9). The maps reveal a similar trend across all nitrogen analyses –concentrations below detection limits to below 10 mg/l at sample locations upgradient of crop fields and CSD, and elevated concentrations at locations downgradient of crop fields and CSD. Results of nitrogen analyses of samples immediately downgradient of the cranberry field in the northwest edge of the study area were below 10 mg/l, and in most cases below 2 mg/l. EPA compared the frequency of exceedances of 10 mg/l for nitrogen analyses from samples downgradient and upgradient of crop fields and CSD. The comparison is summarized in Table 2, below. For this analysis, upgradient samples included samples collected from locations A1-A4, B1, B2, C1, C11, C12, C13, D1, and E10. All other sample locations were considered downgradient of crop fields. Samples collected from locations east-southeast of the CSD facility are potentially downgradient of crop fields and the CSD facility.

Table 2. Frequency of exceedances of 10 mg/l for nitrogen analyses for samples downgradient and upgradient of crop fields.

Nitrogen Analysis Type		Sample depth 20-34' below surface		Sample depth 36-49' below surface	
		Upgradient of Crop Fields	Downgradient of Crop Fields*	Upgradient of Crop Fields	Downgradient of Crop Fields*
EPA UNL Laboratory Nitrate+Nitrite-N Results (Geoprobe)	Number of samples	12	29	12	29
	Nitrate+Nitrite-N results >10 mg/l	0	17	0	17
	exceeding 10 mg/l	0%	59%	0%	59%
EPA Hach Nitrate Test Strip Results (Geoprobe)	Number of samples	12	29	12	29
	Nitrate results >10 mg/l	0	19	0	20
	exceeding 10 mg/l	0%	66%	0%	69%
EPA CRL Nitrate-nitrite N Results (Geoprobe)	Number of samples	11	13	10	13
	Nitrate-nitrite N results >10 mg/l	0	8	0	9
	exceeding 10 mg/l	0%	62%	0%	69%
EPA IC Nitrate-nitrogen Results (Geoprobe)	Number of samples	12	29	12	29
	Nitrate-nitrogen results >10 mg/l	0	19	0	21
	% samples exceeding 10	0%	66%	0%	72%
Total All Nitrogen Analysis Results (Geoprobe)	Number of samples	47	100	46	100
	Results >10 mg/l	0	63	0	67
	exceeding 10 mg/l	0%	63%	0%	67%

* * *

*Groundwater samples collected from locations east-southeast of the CSD facility are potentially downgradient of crop fields and the CSD facility.

According to EPA's nitrogen analyses, summarized above, none of the 93 validated groundwater samples collected upgradient of crop fields exceeded the 10 mg/l nitrate standard. 130 of the 200 (65%) groundwater samples collected downgradient of crop fields exceeded the 10 mg/l nitrate standard. Percentages of groundwater samples collected downgradient of crop fields and exceeding the nitrate standard of 10 mg/l ranged from 59-72%, depending on the type of nitrogen analysis performed. This data suggests crop fields are likely sources of elevated levels nitrogen in groundwater and wells downgradient of crop fields. As discussed above, groundwater samples collected from locations east-southeast of the CSD facility are potentially downgradient of crop fields and the CSD facility.

Synthetic fertilizers and manure are applied to crop fields to improve plant growth. According to the Wisconsin Department of Agriculture, Trade and Consumer Protection's (DATCP) *2016-17 Fertilizer Summary Report*, nitrogen-containing fertilizers, such as urea and UAN solutions, were among the top four most widely consumed agricultural fertilizer in terms of tonnage in Wisconsin (Table 3).

The combination of crop types and high degree of groundwater contamination susceptibility in the study area, along with the common use of nitrogen-based fertilizers, results in a greater potential for nitrate leaching to groundwater (Figure 4).

Figure 4. Nitrate leaching potential (Masarik, 2018).

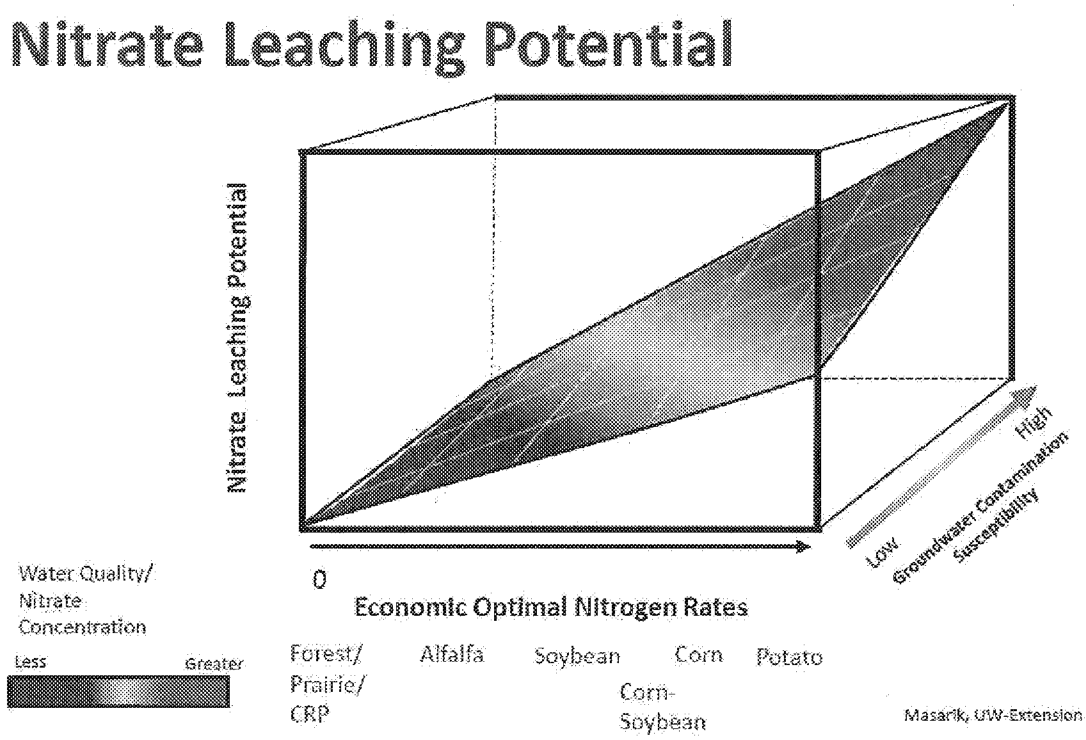


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Table 3. Tonnage of mixed agricultural fertilizer and fertilizer materials by container (DATCP, 2017).

TONNAGE OF MIXED AGRICULTURAL FERTILIZER AND FERTILIZER MATERIALS BY CONTAINER (JULY 2016 - JUNE 2017)				
Fertilizer/Fertilizer Material	Bag	Bulk	Liquid	Total
12-40-0	0	28,749	0	28,749
3-2-1	0	14,741	0	14,741
6-24-6	0	567	10,581	11,148
9-23-30	576	8,167	0	8,743
9-16-31	49	4,363	0	4,412
7-18-6	0	0	4,268	4,268
7-21-7	0	224	3,090	3,314
20-0-0	50	150	3,099	3299
4-10-10	0	769	2,260	3,029
5-14-42	21	2,904	0	2,904
Other Mixed Grades	19,312	134,429	93,132	246,873
Anhydrous Ammonia	0	6,130	23,833	29,963
Ammonium Nitrate	4,854	0	99	5,853
Ammonium Sulfate	301	121,709	573	122,584
28%/32% UAN Solutions	0	33,495	237,219	270,714
Urea	197	240,134	4,579	244,910
Slow Release Urea	0	358	0	358
Ammoniated Phosphates	17	119,246	27,198	146,461
Super Phosphates	0	181	0	181
Bone Meal	0	72	0	72
Rock Phosphates	0	2,201	0	2,201
0-0-60/0-0-62 Muriate of Potash	525	433,315	132	433,972
0-0-50 Sulfate of Potash	254	7,443	0	7,697
0-0-22 Sul-Po Mag	78	6,867	0	6,945
Other N, P & K Sources	27	16,267	21,894	38,188
Natural & Organic (Excluding Bone Meal)	0	33,313	408	33,721
Boron	0	3,126	0	3,126
Gypsum	0	37,304	0	37,304
Calcium (Excluding Lime)	0	1,472	0	1,472
Sulfur (Excluding Gypsum)	0	4,724	0	4,724
Zinc	0	1,750	0	1,750
Other Secondary/Micro-Nutrients (Copper, Iron, Magnesium, Manganese, Molybdenum)	0	803	0	803
Fillers	189	14,099	0	14,288

Anions

The results of major anion analyses conducted, including bromide, chloride, and sulfate, via method 300.0, are summarized in Appendix A, Table A-2. Major anions were analyzed to identify any spatial patterns between sample locations upgradient and downgradient of potential sources.

Bromide

Bromide has been used successfully as a conservative tracer for nitrogen leaching to groundwater in agricultural settings (Kessavalou et.al, 1996; Schuh et.al., 1997). Bromide was detected at low levels in the groundwater, ranging from 0.03-0.17 mg/l throughout the study area. Bromide results were plotted on maps to identify potential spatial patterns. In the deeper sample locations (36-49') bromide shows a pattern of increasing concentration from upgradient borings to boring locations downgradient of CSD and crop fields in the vicinity of CSD (Appendix A, Figure A-10). Bromide results from shallow samples (20-34') show a pattern of increased concentrations downgradient of several crop fields and downgradient of CSD

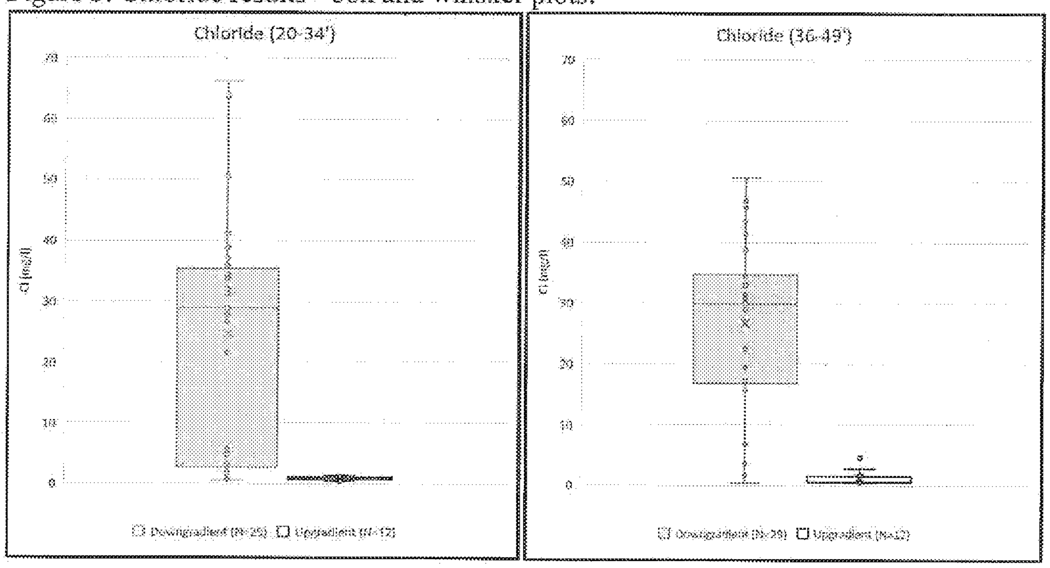
(Appendix A, Figure A-11). Bromide results at all upgradient locations were at the detection limit of 0.03 mg/l.

Chloride

Similar to bromide, chloride is often used as a conservative tracer to study water and contaminant transport in groundwater (Freeze and Cherry 1979). According to DATCP's *2016-17 Fertilizer Summary Report*, Muriate of Potash (potassium chloride), was the most widely consumed agricultural fertilizer in terms of tonnage in Wisconsin (see Table 3 above). Chloride was detected in the groundwater at concentrations ranging from 0.48-66.2 mg/l throughout the study area. The chloride box and whisker plot (Figure 3) summarize the distribution of chloride at downgradient and upgradient locations, at 20-34' and 36-49' depths.

Chloride results were plotted on maps to identify potential spatial patterns. In the deeper sample locations (36-49') chloride shows a pattern of increasing concentration from upgradient borings to boring locations downgradient of crop fields (Appendix A, Figure A-12). Chloride results from shallow samples (20-34') show a similar pattern of increased concentrations downgradient of several crop fields (Appendix A, Figure A-13). Chloride results at all upgradient locations were below 5 mg/l. The average concentration of chloride at downgradient locations was 25.7 mg/l. Review of chloride data shows lower concentrations upgradient of crop fields and elevated chloride levels in downgradient borings and wells. Samples collected from locations east-southeast of the CSD facility are downgradient of crop fields and the CSD facility.

Figure 3. Chloride results - box and whisker plots.



Sulfate

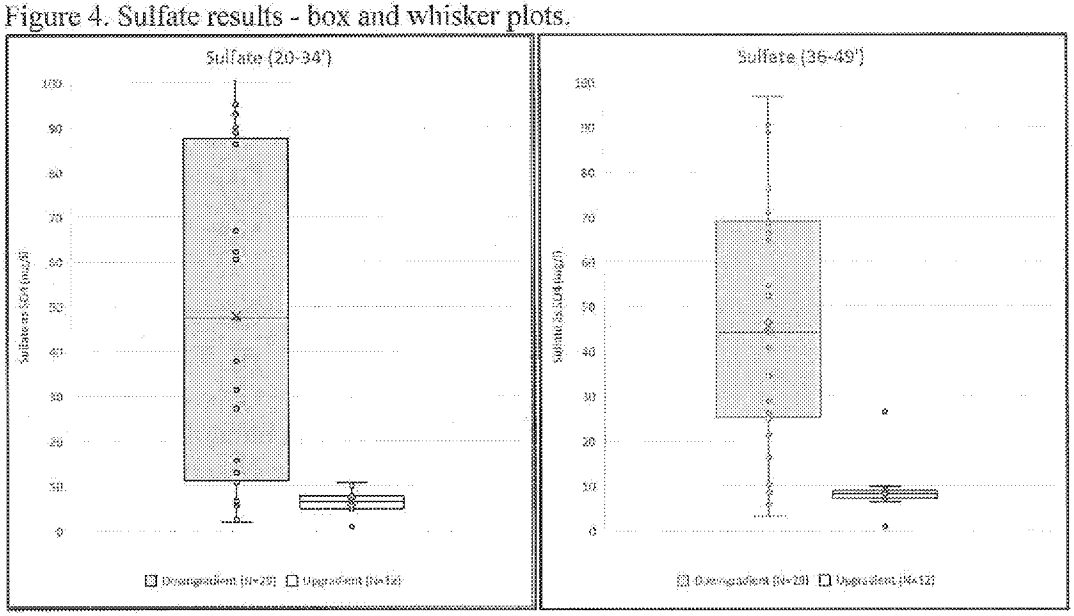
Sulfur is a nutrient that may be deficient in agricultural fields with sandy soils (Laboski, Peters, and Bundy, 2006). To address sulfur deficiencies, sulfate-containing fertilizers and/or manure are applied to crop fields. According to DATCP's *2016-17 Fertilizer Summary Report*, a number of sulfate-containing fertilizers are consumed in Wisconsin, including ammonia sulfate,

sulfate of potash, and sulfur. Ammonia sulfate was the sixth most widely consumed agricultural fertilizer in terms of tonnage in Wisconsin (see Table 3, above).

Sulfate was detected in the groundwater at concentrations ranging from 0.91-112 mg/l throughout the study area. The sulfate box and whisker plot (Figure 4) summarize the distribution of sulfate at downgradient and upgradient locations, at 20-34' and 36-49' depths. Sulfate results at all upgradient locations were below 27 mg/l, with an average concentration of 7.80 mg/l. The average concentration of sulfate at downgradient locations was 46.9 mg/l. Sulfate results were plotted on maps to identify potential spatial patterns. Sulfate results from both deep (36-49'), and shallow (20-34') locations show a similar pattern of increasing concentration from upgradient borings to boring locations downgradient of crop fields (Appendix A, Figures A-14 and A-15).

Review of sulfate data shows lower concentrations upgradient of crop fields and elevated sulfate levels in downgradient borings and wells. Samples collected from locations east-southeast of the CSD facility are downgradient of crop fields and the CSD facility.

Figure 4. Sulfate results - box and whisker plots.



Total Dissolved Solids

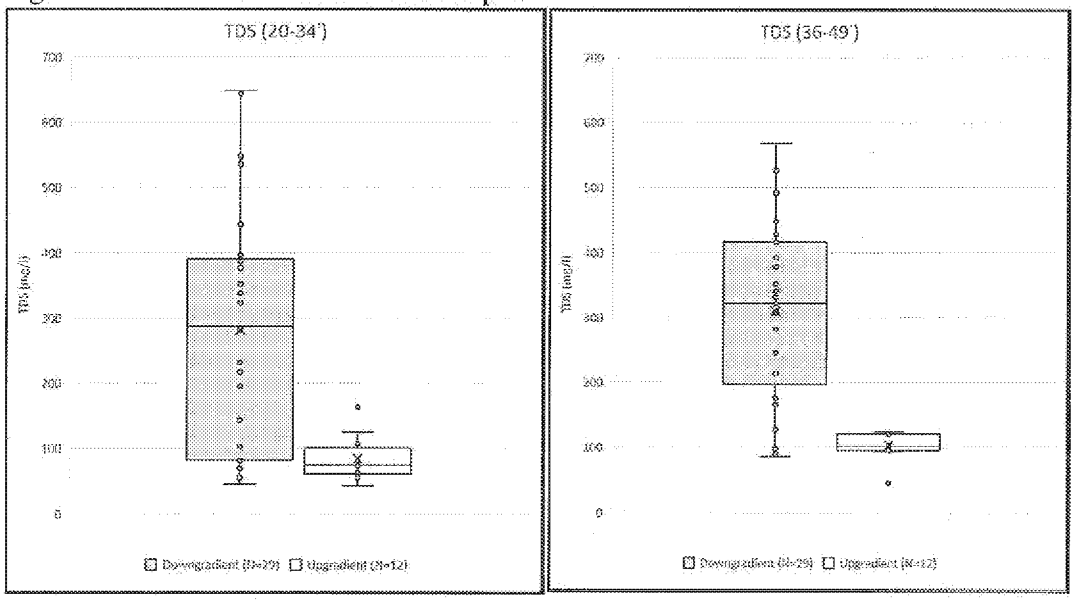
Total dissolved solids (TDS) represent the total concentration of dissolved solids in groundwater samples, and include cations and anions such as nitrates, chlorides and sulfates. Consistent with the results of nitrate, chlorides and sulfates discussed above, TDS concentrations increased from upgradient borings to boring locations downgradient of crop fields.

TDS was detected in the groundwater at concentrations ranging from 44-648 mg/l throughout the study area. The TDS box and whisker plot (Figure 5) summarize the distribution of TDS at downgradient and upgradient locations, at 20-34' and 36-49' depths. TDS results at all upgradient locations were below 165 mg/l, with an average concentration of 93.8 mg/l. The average concentration of TDS at downgradient locations was 310 mg/l. TDS results were plotted on maps to identify potential spatial patterns. TDS results from both deep (36-49') and shallow

(20-34') samples show a similar pattern of increasing concentration from upgradient borings to boring locations downgradient of crop fields (Appendix A, Figures A-16 and A-17).

Similar to results of nitrogen and anion analyses discussed above, review of TDS data suggests crop fields are likely sources of elevated TDS levels in borings and wells downgradient of crop fields. Samples collected from locations east-southeast of the CSD facility are downgradient of crop fields and the CSD facility.

Figure 5. TDS results - box and whisker plots.



N15 and O18 Isotopes

Groundwater samples from all boring locations were submitted to the UNL Laboratory for δ15N-NO3N and δ18O-NO3N isotope analysis, including analysis of nitrate-N concentrations. The complete UNL isotopic analysis report ("Isotope Report"), *Nitrate-N Isotope Results and Interpretation* (Snow, 2018), is provided in Appendix B. The Isotope Report describes the stable isotope analysis of nitrate as follows:

> Nitrate (NO3) is composed of multiple stable isotopes of nitrogen and oxygen, and the composition or proportion of these isotopes changes in a predictable way in surface and groundwater systems. Moreover, nitrogen from specific sources has been shown to have a unique isotope composition or "fingerprint" which has led to a number of studies investigating the utility of linking nitrogen sources to nitrate contamination. The conventional method for measuring and reporting the stable isotope composition uses a delta (δ) notation based on the following equation:

$$\delta(o/oo) = \frac{R_{sample} - R_{air}}{R_{air}} \times 1000$$

where "R" is the measured isotope ratio of the less abundant isotope over the more abundant isotope for a sample and standard (air). In the case of nitrogen, "air" or atmospheric nitrogen gas is used as the reference standard with a very constant 15N composition of 0.366% (Junk and Svec, 1958). The reference for oxygen isotopes is standard mean ocean water (SMOW) with a 18O/16O = 2005.2 ppm.

Stable Isotope "Fingerprinting" of Nitrate

Nitrogen in commercial fertilizers (urea and anhydrous ammonia) has an isotope composition very similar to atmospheric nitrogen, and typically ranges from -6 to +6 per mil (‰) (Kendall, Elliott, et al., 2008). Extensive data collection and analysis of fertilizer sources has suggested that the isotope composition of the majority (~80%) of inorganic nitrogen fertilizer sources ranges between -3 and +3‰ (Michalski, Kolanowski, et al., 2015). In comparison, nitrogen from animal manure, sewage or biosolids tends to be enriched in the heavier 15N isotope, especially after deposition and conversion to the highly volatile ammonia (Kendall, Elliott et al. 2008), and its range tends to be significantly higher, typically between +10 and +25‰. Oxygen isotopes in nitrate, may either originate from the oxygen in a commercial nitrate fertilizer (KNO3 or N2H4O3) or from oxygen atoms in the soil, air, and water during nitrification of ammonia. Because the oxygen isotope composition in air is relatively constant (+22 to +24‰), and the oxygen isotope composition of water changes in a predictable way (usually -5 to -20‰), it is possible to predict the oxygen isotope composition of soil nitrate formed by nitrification.

Both the nitrogen and oxygen isotope composition can be changed in nitrate by another process called microbial denitrification, changes nitrate to nitrite, nitrous oxide, and may eventually convert nitrate to nitrogen gas and water. Because the change in composition is predictable, simultaneous measurement of both nitrogen and oxygen isotopes can provide clues about the source(s) of nitrogen, timing of nitrification (nitrate formation), and whether denitrification has helped to remove any nitrate. As figure 1 [of Isotope Report] indicates, however, the use of both nitrogen and oxygen isotopes for distinguishing sources of nitrate in groundwater can be complicated by multiple sources (atmospheric, manure, septic systems) and processes.

Finally, interpretation of the measured isotope composition of nitrate in groundwater samples with respect to potential sources should include consideration of the expected ranges from sources, potential for mixing multiple nitrogen sources, and the possibility of changes in the isotope composition due to biogeochemical processes (Kendall and Aravena, 2000). While this is often challenging, comparing the measured isotope composition of nitrate with other

> parameters, such as dissolved oxygen, iron, chloride and alkalinity, can help support interpretations.

The Isotope Report includes a plot (Figure 6, below) of δ15N-NO3N versus δ18O-NO3N compared to expected ranges from commercial fertilizer sources, manure and septic sources and inorganic nitrate fertilizers. Note that this analysis cannot distinguish between manure and septic system effluent sources. The Isotope Report describes the plot and related trends as follows:

> Only 1 sample plots in the isotope range inorganic nitrate fertilizers, while over 50% of the samples plot in the range expected for nitrification of commercial nitrogen fertilizer. Roughly one-third of the isotope results fall in the range expected for manure and septic system nitrogen, and several points are consistent with enrichment due to denitrification (Kendall, Elliott, et al., 2008).

Spatial distribution of expected source ranges from both deep (36-49'), and shallow (20-34'), samples is provided in Appendix A, Figures A-18 and A-19.

Nitrogen isotope results from two sample locations with nitrate concentrations above 10 ppm (D8a and E8b), indicate potential manure and/or septic effluent sources of nitrogen. Both locations are immediately downgradient of crop fields and over 4,000 feet downgradient of the nearest residential property. Nitrogen isotope results from three sample locations with nitrate concentrations above 10 ppm (C5Ab, D11b, and E7a), indicate potential nitrification of commercial nitrogen fertilizer, and manure and/or septic effluent sources of nitrogen. All three locations are immediately downgradient of crop fields and over 2,000 feet downgradient of the nearest residential property.

Since isotopic analysis cannot differentiate between human and nonhuman waste, both could be sources of the nitrate in samples C5Ab, D8a, D11b, E7a and E8b and based on the isotopic analysis.

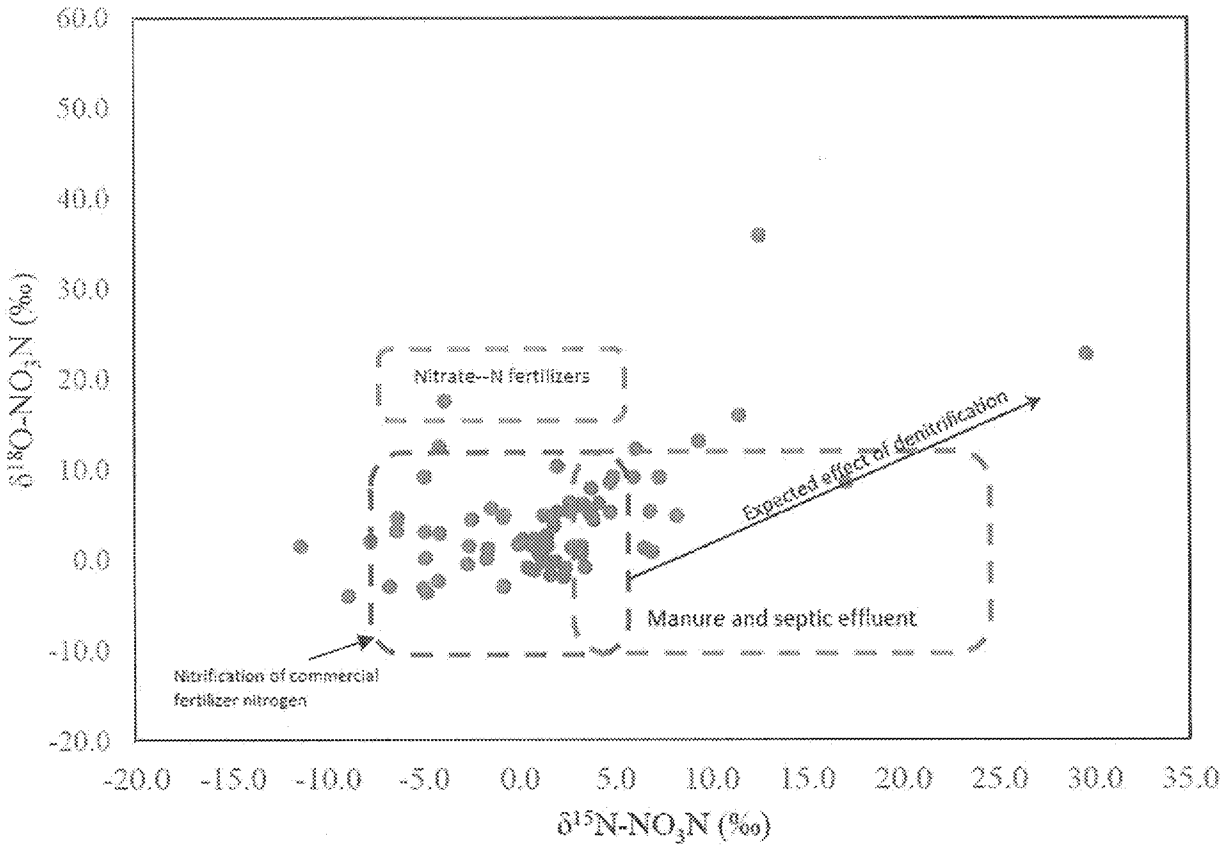
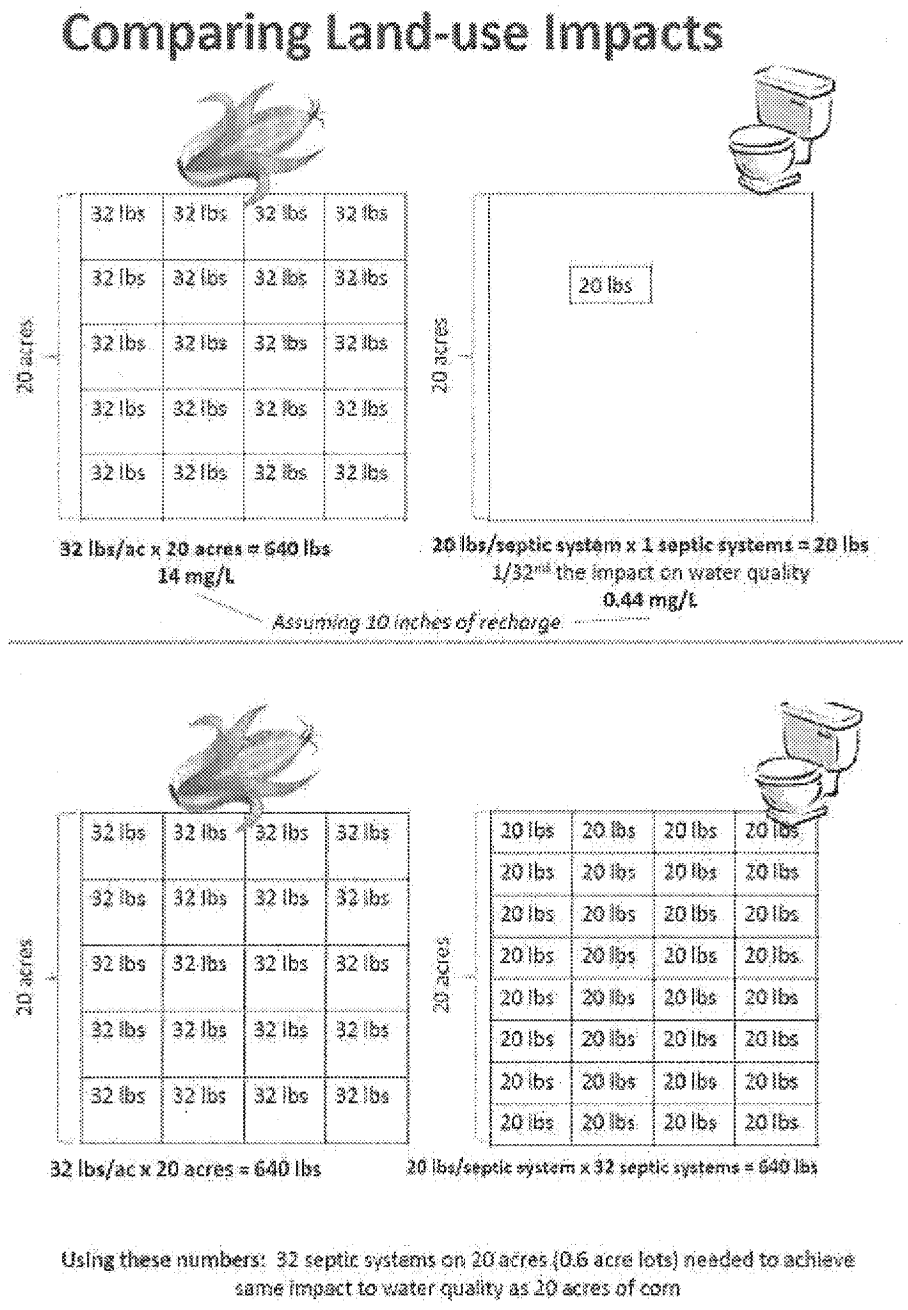


Figure 6. Measured δ15N-NO3N versus δ18O-NO3N compared to expected ranges from commercial fertilizer sources (dark blue dashed box), manure and septic sources (orange dashed box) and inorganic nitrate fertilizers (green box). Source ranges from Kendall and Aravena (2000). [Adapted from Snow, 2018].

The results of the isotopic analysis are consistent with research that suggests agricultural inputs are the most significant in terms of sources of nitrate contamination in groundwater (Shaw, 1994; Masarik, et. al, 2014). As shown in the example in Figure 7, below, residential septic systems can be sources of elevated nitrogen, equivalent to a 20-acre corn field, in cases where homes are concentrated (32 septic systems on 20 acres). However, only three sample locations with nitrate concentrations above 10 ppm and with isotope results indicating potential manure and/or septic effluent sources (C5A, E7, and E8), are potentially downgradient of clusters of homes. Each of the three sample locations are a minimum of 2,000 feet downgradient and within one mile of a cluster of homes (approximately 4-10 homes at each cluster), and separated from homes by crop fields.

Figure 7. Nitrogen impacts to groundwater: corn field versus septic system effluent (Masarik, 2016).



*Tri-State Water Quality Council. 2005. Septic system impact on surface waters: A review for the inland northwest.
**U.S. EPA. 2003. On-site wastewater treatment manual. 625/R-00/008.

VI. SUMMARY

- Portions of northeast Juneau County are areas "more susceptible" to groundwater contamination based on five physical resource characteristics, including depth to bedrock, type of bedrock, soil characteristics, depth to water table and characteristics of surficial deposits (see Figure 3; Schmidt, 1987).

- Agricultural land use in the study area is dominated by cropland and includes a concentrated animal feeding operation (CSD), and cranberry operations (Figure A-1). As summarized in Figure 2, corn, dry beans, and potatoes are the dominant crop type in the study area (USDA, 2018).

- Synthetic fertilizers and manure are applied to crop fields to improve plant growth. According to documents provided by CSD and WDNR, CSD applied fertilizers including ammonium sulfate, aspire, potash, Cal-Sul, 32% UAN (Liquid 32-0-0), Corn Popper (different analysis), and Potato Starter. According DATCP's *2016-17 Fertilizer Summary Report*, nitrogen-containing fertilizers, such as urea and UAN solutions, were among the top four most widely consumed agricultural fertilizer in terms of tonnage in Wisconsin (Table 3).

- The combination of crop types and high degree of groundwater contamination susceptibility in the study area, along with the common use of nitrogen-based fertilizers, results in a greater potential for nitrate leaching to groundwater (Figure 4).

- According to EPA's nitrogen analyses, none of the 93 groundwater samples collected upgradient of crop fields exceeded the 10 mg/l nitrate standard. 130 of the 200 (65%) groundwater samples collected downgradient of crop fields exceeded the 10 mg/l nitrate standard. This data shows elevated levels of nitrogen in groundwater down gradient of crop fields. As discussed above, groundwater samples collected from locations east-southeast of the CSD facility are potentially downgradient of crop fields and the CSD facility.

- Bromide results from shallow samples (20-34') show a pattern of increased concentrations downgradient of several crop fields and downgradient of CSD. In the deeper sample locations (36-49') bromide shows a pattern of increasing concentration from upgradient borings to boring locations downgradient of CSD and crop fields in the vicinity of CSD.

- Chloride data shows lower concentrations upgradient of crop fields and elevated chloride levels in downgradient borings and wells. Chloride samples collected from locations east-southeast of the CSD facility are potentially downgradient of crop fields and the CSD facility.

- Sulfate results show a similar pattern of increasing concentration from upgradient borings to boring locations downgradient of crop fields. Sulfate samples collected from locations east-southeast of the CSD facility are potentially downgradient of crop fields and the CSD facility.

- TDS results show a similar pattern of increasing concentration from upgradient borings to boring locations downgradient of crop fields. TDS samples collected from locations east-southeast of the CSD facility are potentially downgradient of crop fields and the CSD facility.

- Over 50% of the δ15N-NO3N and δ18O-NO3N isotope sample results plot in the range expected for nitrification of commercial nitrogen fertilizer. Roughly one-third of the isotope results fall in the range expected for manure and septic system nitrogen, and several points are consistent with enrichment due to denitrification (Kendall, Elliott, et al., 2008).

- Isotope data and spatial analysis of proximity of sample locations to homes with septic systems suggest any potential impact of septic systems would be limited to three sample locations. Any potential contribution of septic systems to elevated nitrates in groundwater may be further limited as the three sample locations are a minimum of 2,000 feet downgradient of the nearest residential home cluster.

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Appendix A – Tables and Figures

Table A-1. Comparison of the CRL Methods Nitrate-Nitrite N, Nitrate-N with UNL Nitrate + Nitrite-N and Hach® Nitrate Test Strips

SAMPLENAME	LABSAMPID	CRL'NO3NO2N Result D7781-14 (mg/L) - Gallery	CRL Nitrate - N Result (mg/L) - IC Calculated	Abs difference	pH (SU) of the CRL Nitrate-Nitrite Nitrogen results D7781-14 (mg/L) - Gallery samples	UNL Nitrate+Nitrite-N (mg/L) 353.2 Method	EPA Field Data Nitrate (mg/L) Hach Nitrate Test Strips
A1a	1805005-01	0.0738 (U)*	0.06102	0.01	2	*0.000	5
A1b	1805005-02	1.79	1.34244	0.45	2	0.052	3
A2a	1805005-03	36.9	0	36.90	2	*0.000	0
A2b	1805005-04	0.03411 (U)*	0.0122266	0.02	2	*0.006	1
A3a	1805005-05	0.00583 (U)*	0	0.01	2	0.021	1
A3b	1805005-06	0.12	0.05424	0.07	2	0.047	0
A4a	1805005-10	1.25	0.88366	0.37	2	0.568	2
A4b	1805005-11	4.61	4.3166	0.29	2	0.124	4
B1a	1805005-12	0.02071 (U)*	0	0.02	3	0.018	0
B1b	1805005-13	0.04143 (U)*	0.0113226	0.03	2	0.043	0
B2a	1805005-14	0.02529 (U)*	0	0.03	2	*0.000	0
B2b	1805005-15	0.23	0.14012	0.09	2	0.082	0
B3a	1805005-16	4.53	4.0454	0.48	2	1.28	5
B3b	1805005-17	0.96	0.56726	0.39	2	*0.000	2
B4a	1805005-18	33.3	27.12	6.18	2	17.5	50

SAMPLENAME	LABSAMPID	CRL'NO3NO2N Result D7781-14 (mg/L) - Gallery	CRL Nitrate - N Result (mg/L) - IC Calculated	Abs difference	pH (SU) of the CRL Nitrate-Nitrite Nitrogen results D7781-14 (mg/L) - Gallery samples	UNL Nitrate+Nitrite-N (mg/L) 353.2 Method	EPA Field Data Nitrate (mg/L) Hach Nitrate Test Strips
B4b	1805005-19	28.0	17.3568	10.64	2	8.81	20
C1a	1805005-20	0.12	0.0791	0.04	2	9.08	0
C1b	1805005-21	0.02426 (U)*	0.05198	0.03	2	0.44	0
C2a	1805005-22	42.1	36.16	5.94	2	22.8	50
C2b	1805005-23	3.39	2.7572	0.63	2	0.866	10
C3a	1805005-24	27.7	23.278	4.42	2	9.08	20
C3b	1805005-25	2.62	1.72212	0.90	2	0.44	3
C5Aa	1805005-26	44.3	38.42	5.88	2	13.1	20
C5Ab	1805005-27	59.2	62.602	3.40	2	22	50
C6a	1805005-28	36.8	38.42	1.62	2	15.1	50
C6b	1805005-29	25.3	25.312	0.01	3	11.7	50
C7a	1805005-30	31.7	34.126	2.43	2	19.5	50
C7b	1805005-31	37.3	37.968	0.67	2	14.7	50
C8a	1805005-35	17.1	18.193	1.09	2	6.64	20
C8b	1805005-36	2.95	2.486	0.46	2	2.39	5
C9a	1805005-37	2.48	2.2826	0.20	2	2.47	2

SAMPLENAME	LABSAMPID	CRL'NO3NO2N Result D7781-14 (mg/L) - Gallery	CRL Nitrate - N Result (mg/L) - IC Calculated	Abs difference	pH (SU) of the CRL Nitrate-Nitrite Nitrogen results D7781-14 (mg/L) - Gallery samples	UNL Nitrate+Nitrite-N (mg/L) 353.2 Method	EPA Field Data Nitrate (mg/L) Hach Nitrate Test Strips
C9b	1805005-38	0.69	0.565	0.13	2	0.646	2
C10a	1805005-39	8.33	6.893	1.44	2	7.76	5
C10b	1805005-40	16.7	16.95	0.25	2	15.6	20
C11a	1805005-41	0.00348 (U)*	0	0.00	3	*0.000	0
C11b	1805005-42	0.57	0.34804	0.22	2	0.119	1
C12a	1805005-43	0.02879 (U)*	0	0.03	2	*0.000	0
C12b	1805005-44	0.05712 (U)*	0	0.06	2	*0.000	0
C13a	1805005-45	0.02451 (U)*	0	0.02	3	*0.000	0
C13b	1805005-46	0.02199 (U)*	0	0.02	2	*0.000	0
D1a	1805005-47	-0.01954 (U)*	0	0.02	2	*0.000	0
D1b	1805005-48	0.02459 (U)*	0	0.02	3	*0.000	0
D2a	1805005-49	2.86	2.5538	0.31	3	1.65	5
D2b	1805005-50	32.7	33.9	1.20	2	13.5	50
D3a	1805005-51	21.1	21.7638	0.66	2	8.98	20
D3b	1805005-52	23.4	22.2836	1.12	2	13.1	50
D4a	1805005-53	20.5	21.4022	0.90	2	10.2	20

SAMPLENAME	LABSAMPID	CRL'NO3NO2N Result D7781-14 (mg/L) - Gallery	CRL Nitrate - N Result (mg/L) - IC Calculated	Abs difference	pH (SU) of the CRL Nitrate-Nitrite Nitrogen results D7781-14 (mg/L) - Gallery samples	UNL Nitrate+Nitrite-N (mg/L) 353.2 Method	EPA Field Data Nitrate (mg/L) Hach Nitrate Test Strips
D4b	1805005-54	50.6	55.37	4.77	2	17.7	50
D5a	1805007-01	0.29	0.47686	0.19	1	0.451	2
D5b	1805007-02	1.36	1.52324	0.16	1	1.18	2
D6a	1805007-03	-0.06753 (U)*	49.042	49.11	1	41.1	50
D6b	1805007-04	-0.01465 (U)*	26.894	26.91	1	24.5	50
D7a	1805007-08	-0.06481 (U)*	37.968	38.03	1	30.7	50
D7b	1805007-09	36.8	39.324	2.52	1	32.2	50
D8a	1805007-10	42.3	48.816	6.52	1	48.8	50
D8b	1805007-11	0.03843 (U)*	48.138	48.10	1	39	50
D9a	1805007-12	-0.09567 (U)*	31.414	31.51	1	30.3	20
D9b	1805007-13	2.29	2.8702	0.58	1	1.52	5
D10a	1805007-14	14.3	13.2888	1.01	1	8.79	20
D10b	1805007-16	-0.02915 (U)*	15.142	15.17	1	8.4	20
D11a	1805007-18	32.2	30.284	1.92	1	28	20
D11b	1805007-19	23.9	22.826	1.07	1	14.5	20
E1a	1805007-20	27.2	24.86	2.34	1	11.7	20

SAMPLENAME	LABSAMPID	CRL NO3NO2N Result D7781-14 (mg/L) - Gallery	CRL Nitrate - N Result (mg/L) - IC Calculated	Abs difference	pH (SU) of the CRL Nitrate-Nitrite Nitrogen results D7781-14 (mg/L) - Gallery samples	UNL Nitrate+Nitrite-N (mg/L) 353.2 Method	EPA Field Data Nitrate (mg/L) Hach Nitrate Test Strips
E1b	1805007-21	25.7	23.73	1.97	1	11.8	50
E2a	1805007-22	1.52	1.36956	0.15	1	0.995	2
E2b	1805007-23	3.15	2.825	0.33	1	2.58	2
E3a	1805007-26	6.58	6.1698	0.41	1	3.83	5
E3b	1805007-27	7.40	7.5936	0.19	1	6.14	5
E4a	1805007-28	23.3	22.6	0.70	1	26.1	20
E4b	1805007-29	26.8	25.086	1.71	1	20	20
E5a	1805007-30	38.7	35.03	3.67	1	28.3	50
E5b	1805007-31	26.9	24.408	2.49	1	17.5	20
E6a	1805007-32	0.15	0.14464	0.01	1	0.149	0
E6b	1805007-33	0.15	0.08588	0.06	1	0.093	0
E7a	1805007-34	-0.08565 (U)*	21.47	21.56	1	16.1	20
E7b	1805007-35	-0.03298 (U)*	22.3514	22.38	1	13.8	50
E8a	1805007-36	-0.03298 (U)*	19.097	19.13	1	28.6	20
E8b	1805007-37	-0.11255 (U)*	25.764	25.88	1	21.1	50
E10a	1805007-38	1.13	1.05994	0.07	1	0.427	2

SAMPLENAME	LABSAMPID	CRL'NO3NO2N Result D7781-14 (mg/L) - Gallery	CRL Nitrate - N Result (mg/L) - IC Calculated	Abs difference	pH (SU) of the CRL Nitrate-Nitrite Nitrogen results D7781-14 (mg/L) - Gallery samples	UNL Nitrate+Nitrite-N (mg/L) 353.2 Method	EPA Field Data Nitrate (mg/L) Hach Nitrate Test Strips
E10b	1805007-40	0.06174 (U)*	0.0452	0.02	1	0.042	0
E9a	1805007-43	-0.06142 (U)*	15.9782	16.04	1	20.8	10
E9b	1805007-44	20.2	16.7692	3.43	1	20.2	20

As noted above in Section II, page 3, EPA compared the CRL nitrate-nitrite nitrogen data using ASTM Method D7781-14 to other datasets. Shown below are scatter graphs to evaluate the correlation between this data and CRL's data for nitrate-nitrogen via EPA Method 300.0 and CRL's total dissolved solids data. The correlation coefficient between CRL's ASTM Method D7781-14 and EPA Method 300.0 is .5209 when including all data. However, when the inconsistent data is not plotted, the correlation coefficient is .9784 (Appendix A, Figure A-20. The correlation coefficient of TDS to CRL nitrate-nitrite nitrogen data using ASTM Method D7781-14 is 0.5359. However, when the inconsistent data is not plotted, the correlation coefficient is .9343 (Appendix A, Figure A-21). There is also a strong correlation between EPA Method 300.0 and TDS with a correlation coefficient of .9341 (Appendix A, Figure A-22).

Table A-2: CRL Anion Analyses

Sample ID	Collection Date	Collection Time	Fluoride mg/L	Flags/ Qualifiers	Chloride mg/L	Flags/ Qualifiers	Sulfate as S04 mg/L	Flags/ Qualifiers	Bromide mg/L	Flags/ Qualifiers	Nitrate-Nitrogen	Flags/ Qualifiers
A1a	4/30/2018	7:19 AM	0.06		4.61		7.02		U		0.0609	(H), J
A1b	4/30/2018	7:32 AM	0.03		1.16		5.98		U		1.34	(H), J
A2a	4/30/2018	8:15 AM	0.04		1.21		9.84		U		U	(H), J
A2b	4/30/2018	8:24 AM	0.06		0.85		5.01		U		U	(H), UJ
A3a	4/30/2018	9:06 AM	0.08		0.75		8.79		U		U	(H), U J
A3b	4/30/2018	9:14 AM	0.03		0.77		6.44		U		0.0551	(H), J
A4 Equip	4/30/2018	9:38 AM	0.04		1.00		5.18		U		0.0592	(H), J
A3a (Dup)	4/30/2018	9:06 AM	0.08		0.76		7.98		U		U	(H), UJ
FB1	4/30/2018	9:49 AM	U		U		U		U		U	(H), UJ
A4a	4/30/2018	9:58 AM	0.07		1.01		26.5		U		0.884	(H), J
A4b	4/30/2018	10:09 AM	0.06		0.53		10.7		U		4.31	(H), J
B1a	4/30/2018	10:51 AM	0.08		0.71		8.18		U		U	(H), UJ
B1b	4/30/2018	10:58 AM	0.09		1.10		7.87		U		U	(H), UJ
B2a	4/30/2018	11:40 AM	0.08		2.77		8.81		U		U	(H), UJ
B2b	4/30/2018	11:48 AM	0.04		0.50	J	5.10	J	U		0.140	(H), J
B3a	4/30/2018	12:29	0.05		19.5		26.3		U		4.05	(H), J
B3b	4/30/2018	12:36	0.05		2.09		6.72		U		0.568	(H), J
B4a	4/30/2018	13:10	0.03		35.0		66.3		U		27.1	(E), (H), J
B4b	4/30/2018	13:41	0.10		26.7		112		U		17.4	(H), J
C1a	4/30/2018	15:02	0.03		0.73		7.79		U		0.0799	(H), J
C1b	4/30/2018	15:27	0.03		0.70		6.53		U		0.0515	(H), J
C2a	4/30/2018	16:06	0.03		34.4		29.2		U		36.1	(E), (H), J
C2b	4/30/2018	16:14	0.04		3.33		15.7		U		2.75	(H), J
C3a	4/30/2018	14:16	0.03		30.0		40.9		U		23.2	(E), (H), J
C3b	4/30/2018	14:26	0.03		5.75		11.5		U		1.72	(H), J
C5Aa	5/1/2018	6:29	0.03		38.8		90.4		0.12		38.5	(E), (H), J
C5Ab	5/1/2018	6:43	0.04		50.5		101		0.14		62.6	(E), (H), J
C6a	5/1/2018	7:06	0.03		43.5		54.7		0.16		38.3	(E), (H), J
C6b	5/1/2018	7:15	0.09		29.5		88.9		0.17		25.4	(E), (H), J
C7a	5/1/2018	7:48	0.03		33.6		52.5		0.13		34.0	(E), (H), J
C7b	5/1/2018	8:02	0.04		35.9		95.2		0.15		38.0	(E), (H), J
FB2	5/1/2018	7:39	U		U		U		U		U	(H), UJ
C7 Equip	5/1/2018	7:38	0.02		0.73		1.05		U		U	(H), UJ
C7b Dup	5/1/2018	8:02	0.04		37.3		93.7		0.15		38.8	(E), (H), J
C8a	5/1/2018	8:35	0.05		15.9		44.5	L	U		18.2	H), (MS) J, L
C8b	5/1/2018	8:42	0.04		1.84		15.9		U		2.49	J, (H)
C9a	5/1/2018	10:00	0.05		3.66		16.4		U		2.29	(H), J
C9b	5/1/2018	10:21	U		0.56		6.69		U		0.565	(H), J
C10a	5/1/2018	11:05	0.05		6.93		3.35		U		6.90	(H), J
C10b	5/1/2018	11:12	0.07		31.3		2.03		U		16.9	(H), J
C11a	5/1/2018	11:46	0.04		0.78		8.99		U		U	(H), UJ

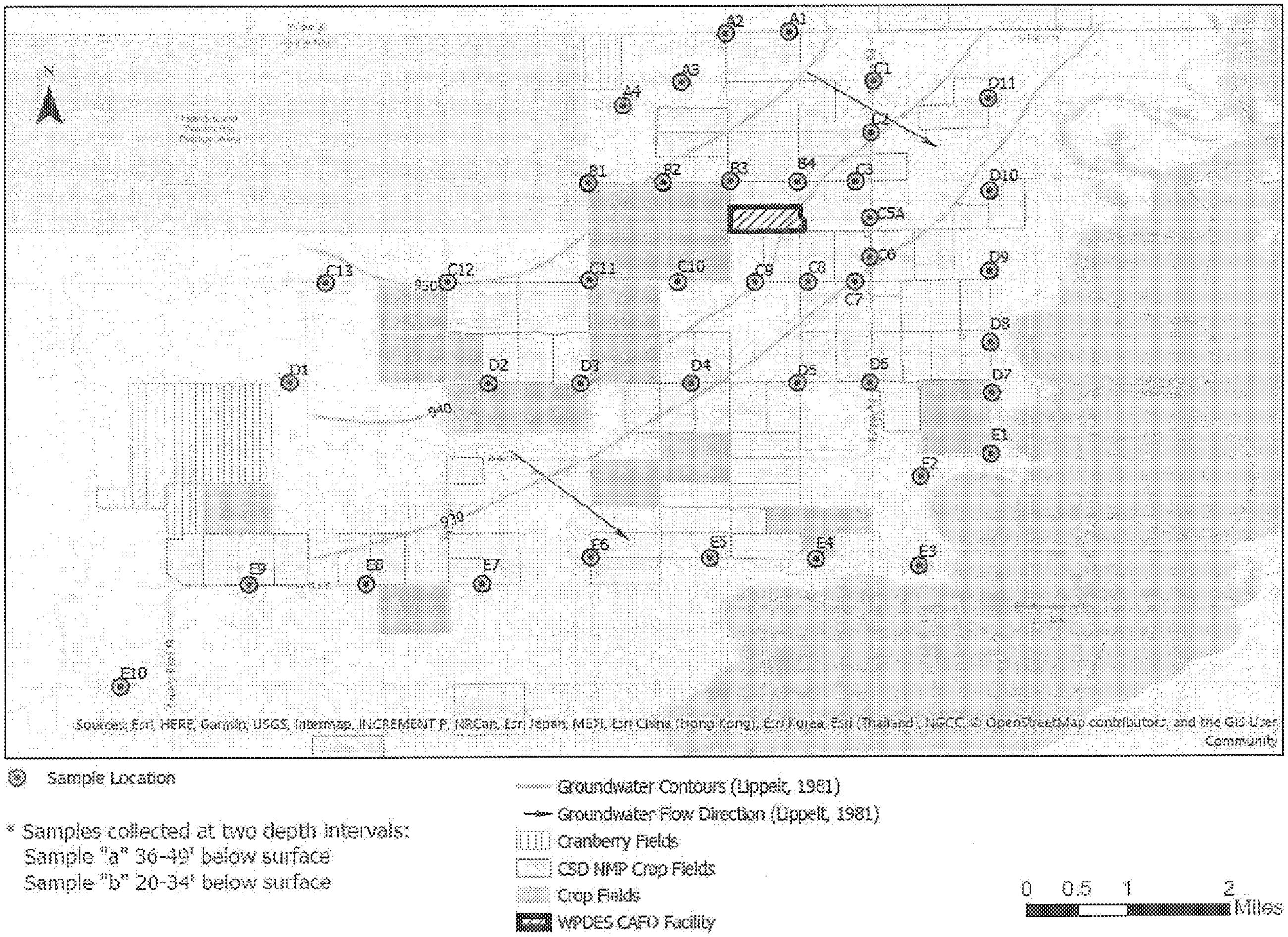
Sample ID	Collection Date	Collection Time	Fluoride mg/L	Flags/ Qualifiers	Chloride mg/L	Flags/ Qualifiers	Sulfate as S04 mg/L	Flags/ Qualifiers	Bromide mg/L	Flags/ Qualifiers	Nitrate-Nitrogen	Flags/ Qualifiers
C11b	5/1/2018	11:52	0.10		0.92		6.69		U		0.347	(H), J
C12a	5/1/2018	12:41	0.09		1.68		0.91		U		U	(H), UJ
C12b	5/1/2018	12:47	0.07		1.34		0.93		U		U	(H), UJ
C13a	5/1/2018	13:30	0.08		0.60		6.46		U		U	(H), UJ
C13b	5/1/2018	13:39	0.11		1.27		7.34		U		U	(H), UJ
D1a	5/1/2018	14:19	0.07		0.53		7.67		U		U	(H), UJ
D1b	5/1/2018	14:26	0.07		0.83		4.92		U		U	(H), UJ
D2a	5/1/2018	15:00	0.06		17.3		44.3		U		2.56	(H), J
D2b	5/1/2018	15:06	0.11		38.8		90.1		0.13		34.0	(E), (H), J
D3a	5/1/2018	15:41	0.06		31.5		25.5		U		21.8	(E), (H), J
D3b	5/1/2018	15:48	0.05		34.4		2.55		U		22.3	(E), (H), J
D4a	5/1/2018	16:19	0.04		29.4		25.1		U		21.4	(E), (H), J
D4b	5/1/2018	16:26	0.05		63.7		93.0		0.15		55.4	(E), (H), J
D5a	5/2/2018	6:38	0.05		1.67		10.3		U		0.477	(H), J
D5b	5/2/2018	6:46	0.04		0.79		6.65		U		1.52	(H), J
D6a	5/2/2018	7:17	U		45.7		96.9		0.13		49.0	(E), (H), J
D6b	5/2/2018	7:29	0.04		27.9		67.0		U		27.0	(E), (H), J
D7Equip	5/2/2018	8:01	0.05		2.07		1.27		U		0.0427	(H), J
FB3	5/2/2018	8:03	U		U		U		U		U	(H), UJ
D7aDup	5/2/2018	8:12	U		47.0		68.5		U		38.2	(E), (H), J
D7a	5/2/2018	8:12	U		46.8	L	68.7	L	U		38.1	(E), (H), (MS), J, L
D7b	5/2/2018	8:19	0.05		41.2		112		U		39.4	(E), (H), J
D8a	5/2/2018	8:55	0.03		50.6		88.8		0.15		48.9	(E), (H), J
D8b	5/2/2018	9:11	0.05		66.2		86.4		0.14		48.2	(E), (H), J
D9a	5/2/2018	9:45	0.03		41.4		71.0		U		31.4	(E), (H), J
D9b	5/2/2018	9:54	0.06		4.86		10.8		U		2.87	(H), J
D10a	5/2/2018	10:29	0.04		22.8		28.9		U		13.3	(H), J
D10aDup	5/2/2018	10:29	0.03		22.9		29.8		U		10.3	(H), J
D10b	5/2/2018	10:41	0.04		21.6		31.6		U		15.1	(H), J
D10bDup	5/2/2018	10:41	0.05		20.6		31.5		U		14.7	(H), J
D11a	5/2/2018	11:19	0.03		22.5	L	21.4	L	U		30.2	(E), (H), (MS), J, L
D11b	5/2/2018	11:42	0.02		34.9	L	60.6	L	U		22.7	(E), (H), J
E1a	5/2/2018	12:41	0.03		33.2		76.3		U		24.8	(E), (H), J
E1b	5/2/2018	12:58	0.06		27.3		38.0		U		23.8	(E), (H), J
E2a	5/2/2018	13:28	0.05		29.0		8.54		U		1.37	(H), J
E2b	5/2/2018	13:37	0.08		1.76		13.0		U		2.83	(H), J
E2aDup	5/2/2018	13:28	0.05		27.6		8.29		U		1.44	(H), J
E2bDup	5/2/2018	13:37	0.07		1.59		12.6		U		2.84	(H), J
E3a	5/2/2018	14:03	0.05		2.01		46.7		U		6.17	(H), J
E3b	5/2/2018	14:09	0.06		0.97		27.4		U		7.60	(H), J
E4a	5/2/2018	14:37	0.04		16.4		71.0	L	U		22.6	(E), (H), (MS), J, L

Sample ID	Collection Date	Collection Time	Fluoride mg/L	Flags/ Qualifiers	Chloride mg/L	Flags/ Qualifiers	Sulfate as S04 mg/L	Flags/ Qualifiers	Bromide mg/L	Flags/ Qualifiers	Nitrate-Nitrogen	Flags/ Qualifiers
E4b	5/2/2018	14:43	0.05		33.7		62.8		U		25.1	(E), (H), J
E5a	5/2/2018	15:08	0.03		30.8		69.3		U		35.1	(E), (H), J
E5b	5/2/2018	15:13	0.04		28.9		61.3		U		24.5	(E), (H), J
E6a	5/2/2018	15:38	0.06		0.48		6.00		U		0.144	(CCV), (H), J, K
E6b	5/2/2018	15:44	0.04		0.69		5.59		U		0.0856	(CCV), (H), J, K
E7a	5/2/2018	16:09	0.02		33.0		41.1		U		21.5	(CCV), (E), (H), J, K
E7b	5/2/2018	16:35	U		32.4		47.5		0.15		22.4	(CCV), (E), (H), J, K
E8a	5/3/2018	8:40	U		26.9		34.6		U		19.1	, K, (CCV), (H)
E8b	5/3/2018	8:48	0.05		37.1		60.6		0.14		25.7	(CCV), (E), (H), J, K
E9a	5/3/2018	9:53	0.06		31.2		64.8		U		16.0	(H), J
E9b	5/3/2018	10:02	0.05		32.1	L	62.3	L	U		16.8	(H), J
E10a	5/3/2018	7:15	0.06		0.58		8.54		U		1.06	(CCV), (H), J, K
E10aDup	5/3/2018	7:15	0.05		0.57		8.23		U		1.01	(CCV), (H), J, K
E10b	5/3/2018	7:27	0.04		1.05		10.2		U		0.0459	(CCV), (H), J, K
FB4	5/3/2018	7:36	U		U		U		U		U	(CCV), (H), UJ
E10 Equip	5/3/2018	7:13	U		U		U		U		U	(H), UJ

UJ- The analyte was not detected at or above the reported limit. The reported limit is an estimate
L- The identification of the analyte is acceptable; the reported value may be biased low. The actual value is expected to be greater than the reported value
K- The identification of the analyte is acceptable; the reported value may be biased high. The actual value is expected to be greater than the reported value
J- The identification of the analyte is acceptable; the reported value is an estimate
(MS) Matrix spike recovery criteria not met for this analyte
(H) Holding time exceeded for sample preparation and/or analysis; Target analyte concentrations and/or reporting limits may not be accurate
(E) This analyte exceeded calibration range
(CCV) Continuing calibration verification criteria not met for this analyte
U- Not Detected

Figure A-1.

Temporary Groundwater Sample Locations *



* Samples collected at two depth intervals:
Sample "a" 36-49' below surface
Sample "b" 20-34' below surface

Figure A-2.

EPA UNL Nitrate+Nitrite-N Results
(boring groundwater samples 36-49' below surface)

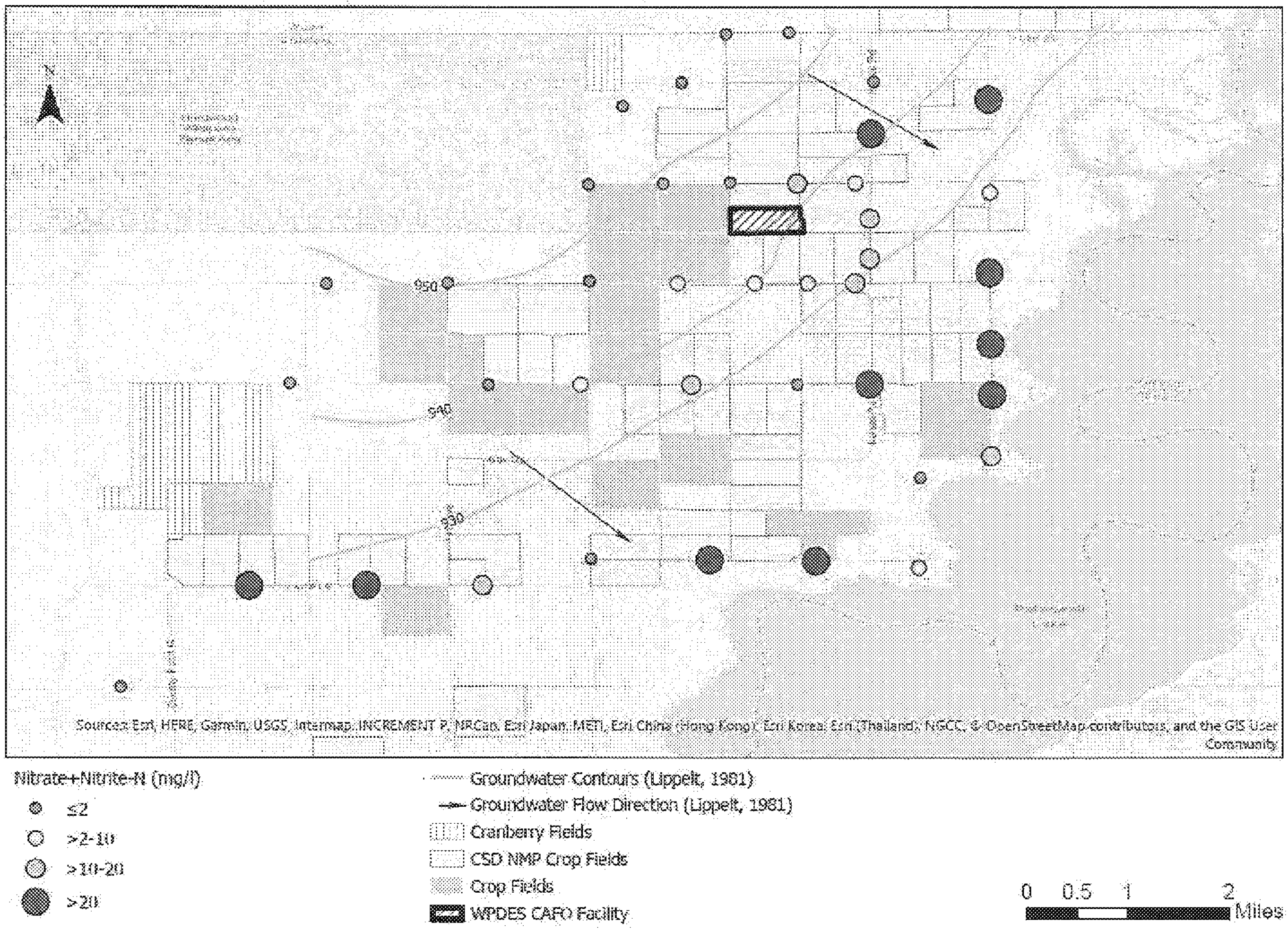


Figure A-3.

EPA UNL Nitrate+Nitrite-N Results
(boring groundwater samples 20-34' below surface)

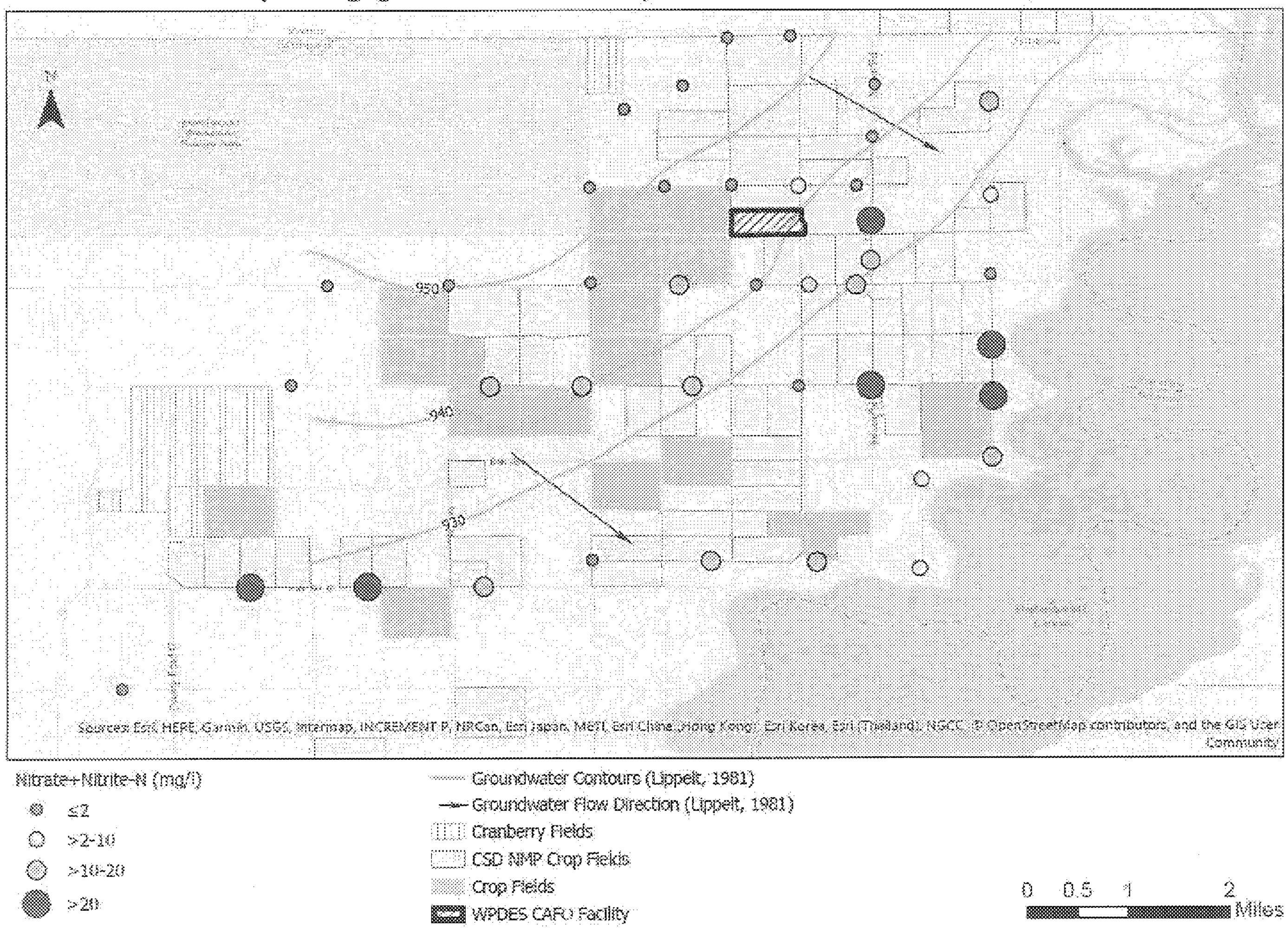
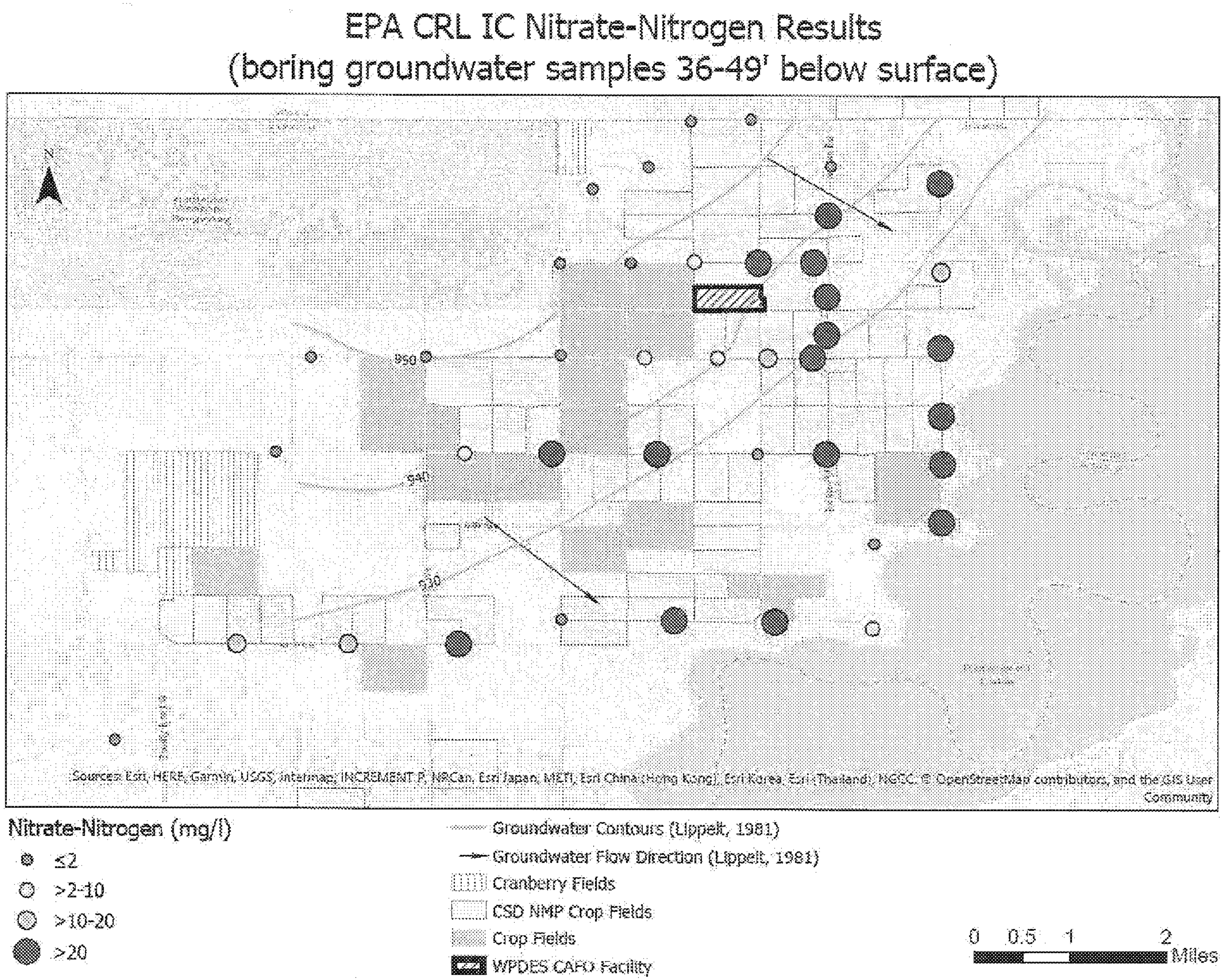
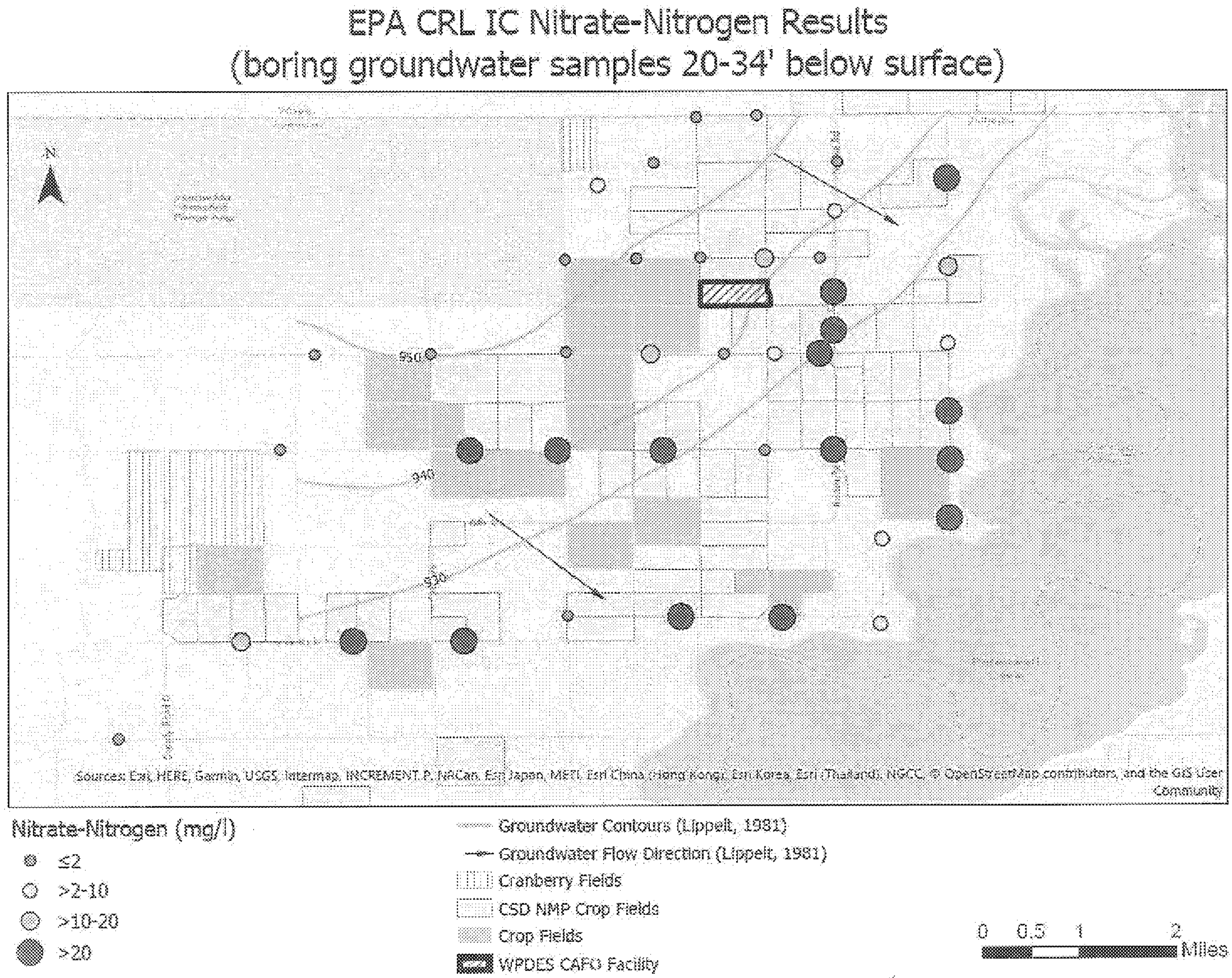


Figure A-4.



ED_004625A_00022255-00036

Figure A-5.



ED_004625A_00022255-00037

Figure A-6.

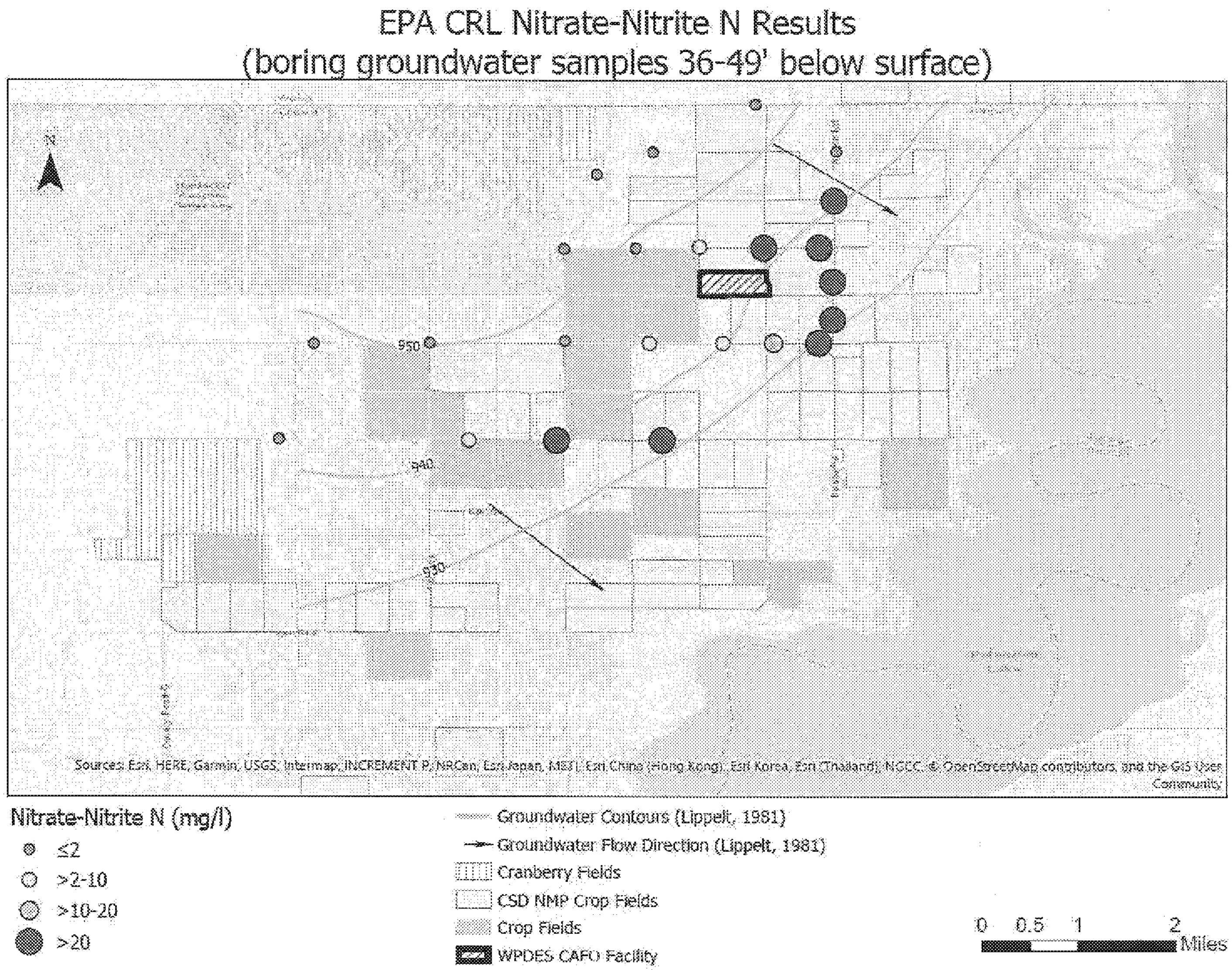

EPA CRL Nitrate-Nitrite N Results
(boring groundwater samples 36-49' below surface)
N
950
940
930
Sources: Esri, HERE, Garmin, USGS, Intermap, INCREMENT P, NRCan, Esri Japan, METI, Esri China (Hong Kong), Esri Korea, Esri (Thailand), NGCC, © OpenStreetMap contributors, and the GIS User Community
Nitrate-Nitrite N (mg/l)
≤2
>2-10
>10-20
>20
Groundwater Contours (Lippelt, 1981)
Groundwater Flow Direction (Lippelt, 1981)
Cranberry Fields
CSD NMP Crop Fields
Crop Fields
WPDES CAFO Facility
0 0.5 1 2
Miles

Figure A-7.

EPA CRL Nitrate-Nitrite N Results
(boring groundwater samples 20-34' below surface)

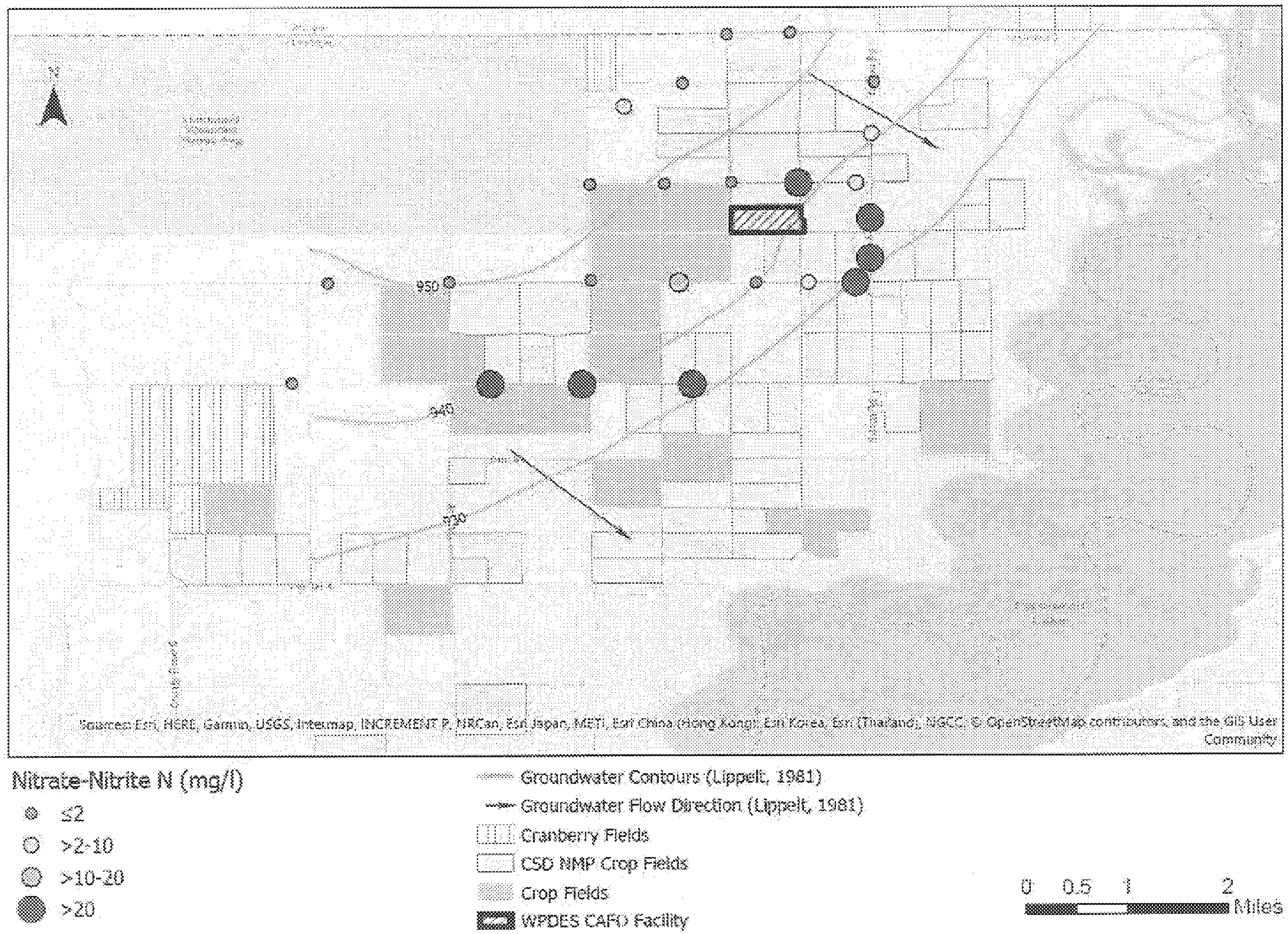
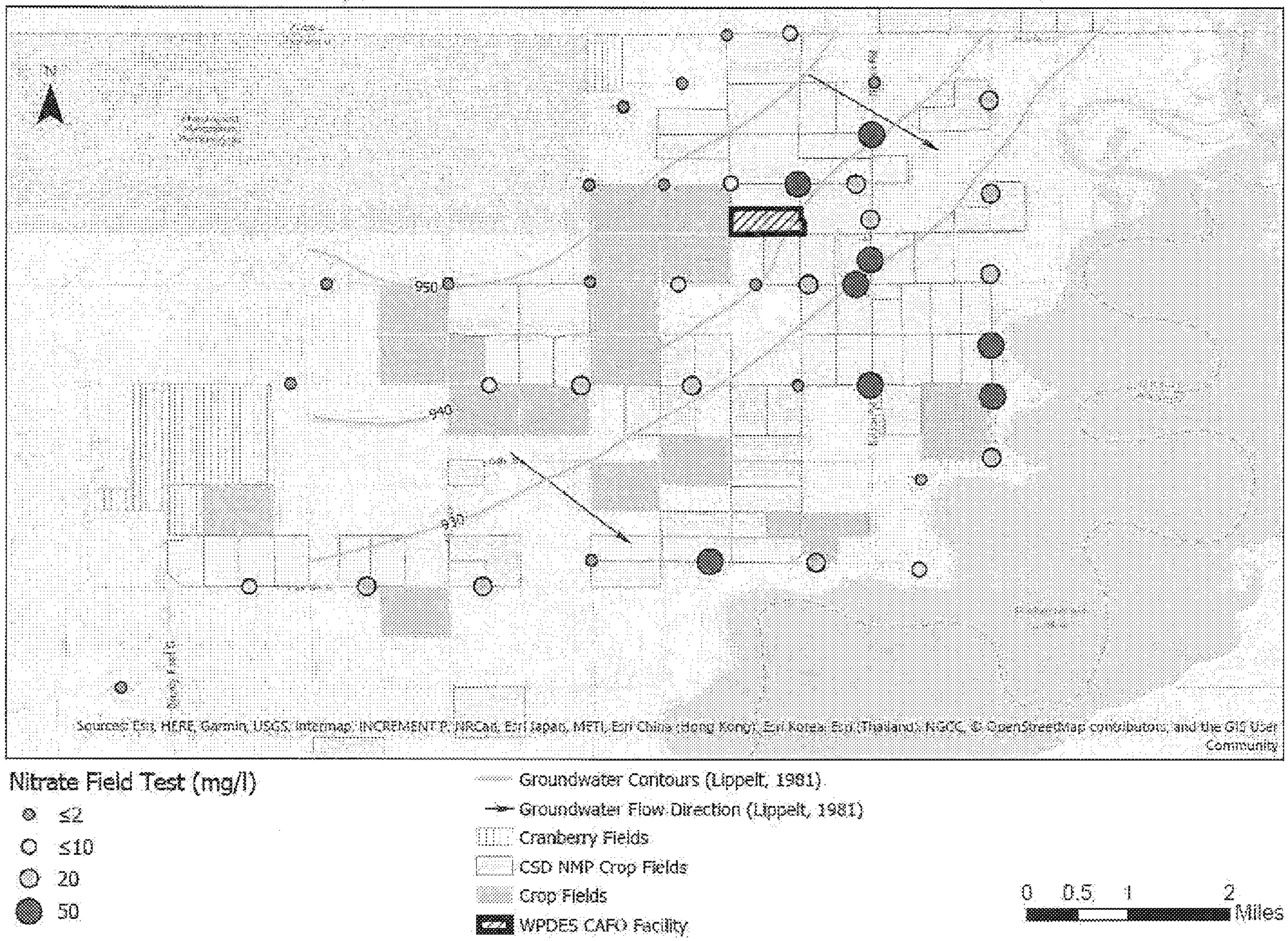


Figure A-8.

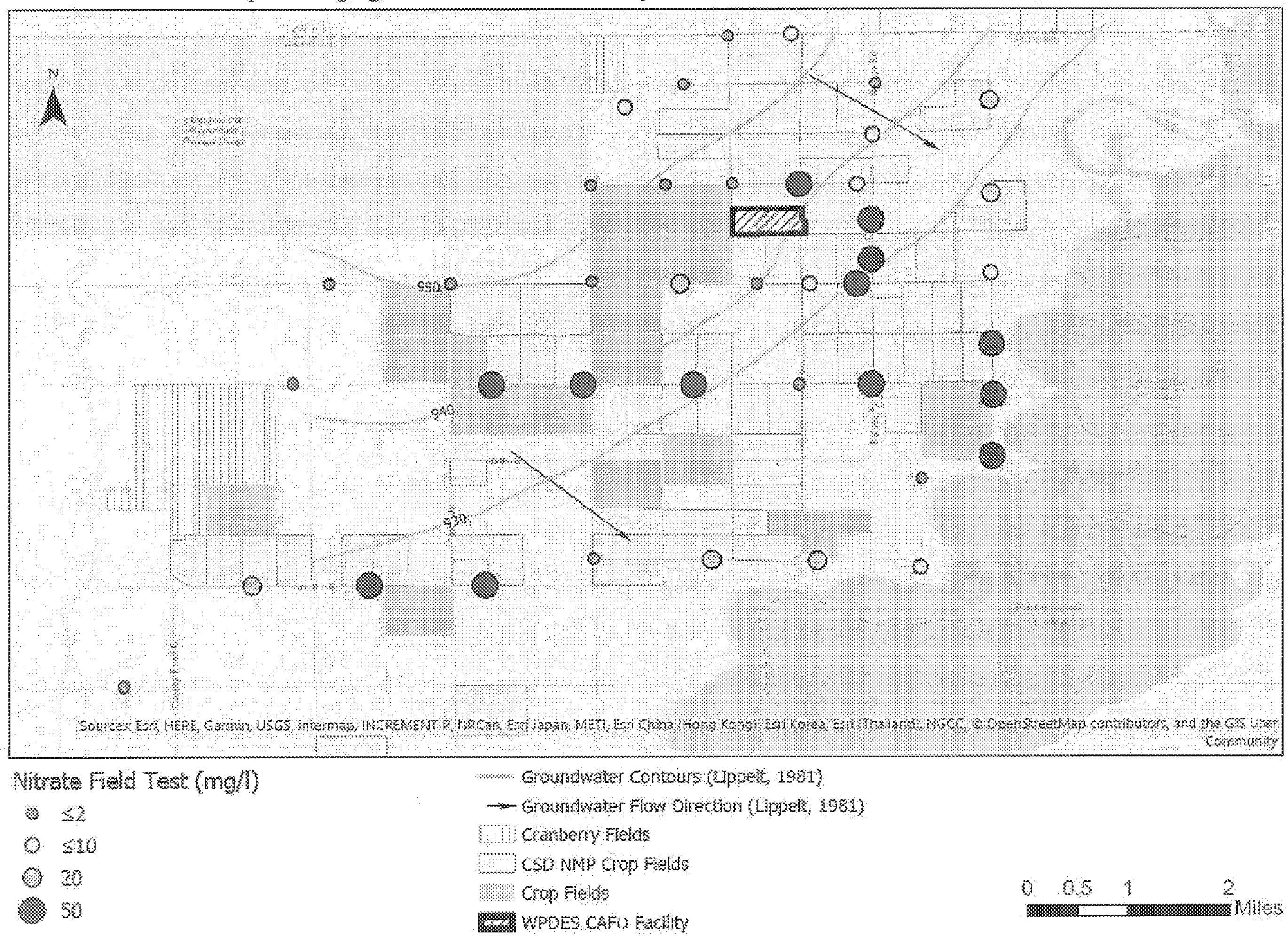
Hach Field Test Strip Nitrate Results
(boring groundwater samples 36-49' below surface)



ED_004625A_00022255-00040

Figure A-9.

Hach Field Test Strip Nitrate Results
(boring groundwater samples 20-34' below surface)



ED_004625A_00022255-00041

Figure A-10.

EPA CRL Bromide Results
(boring groundwater samples 36-49' below surface)

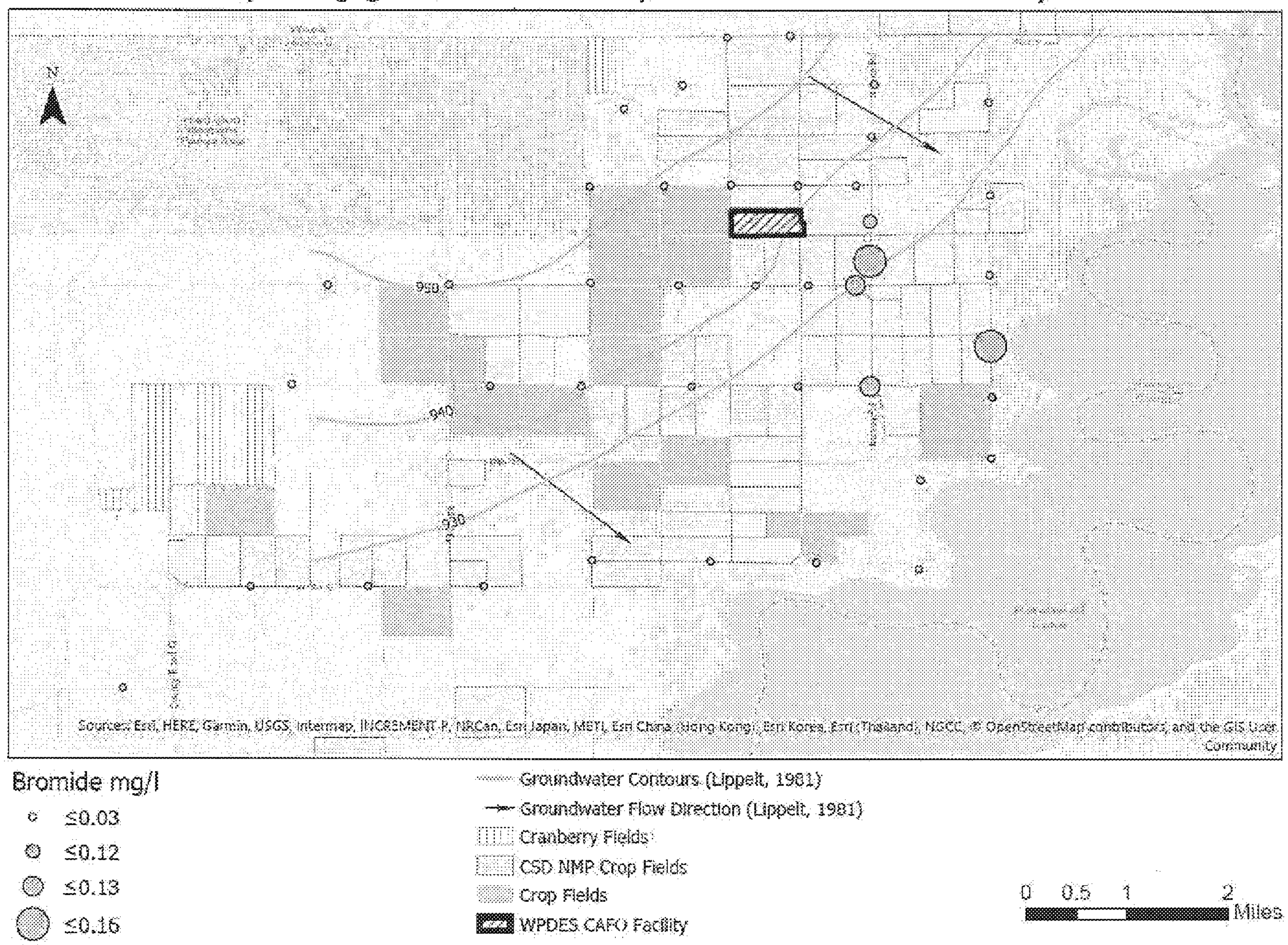


Figure A-11.

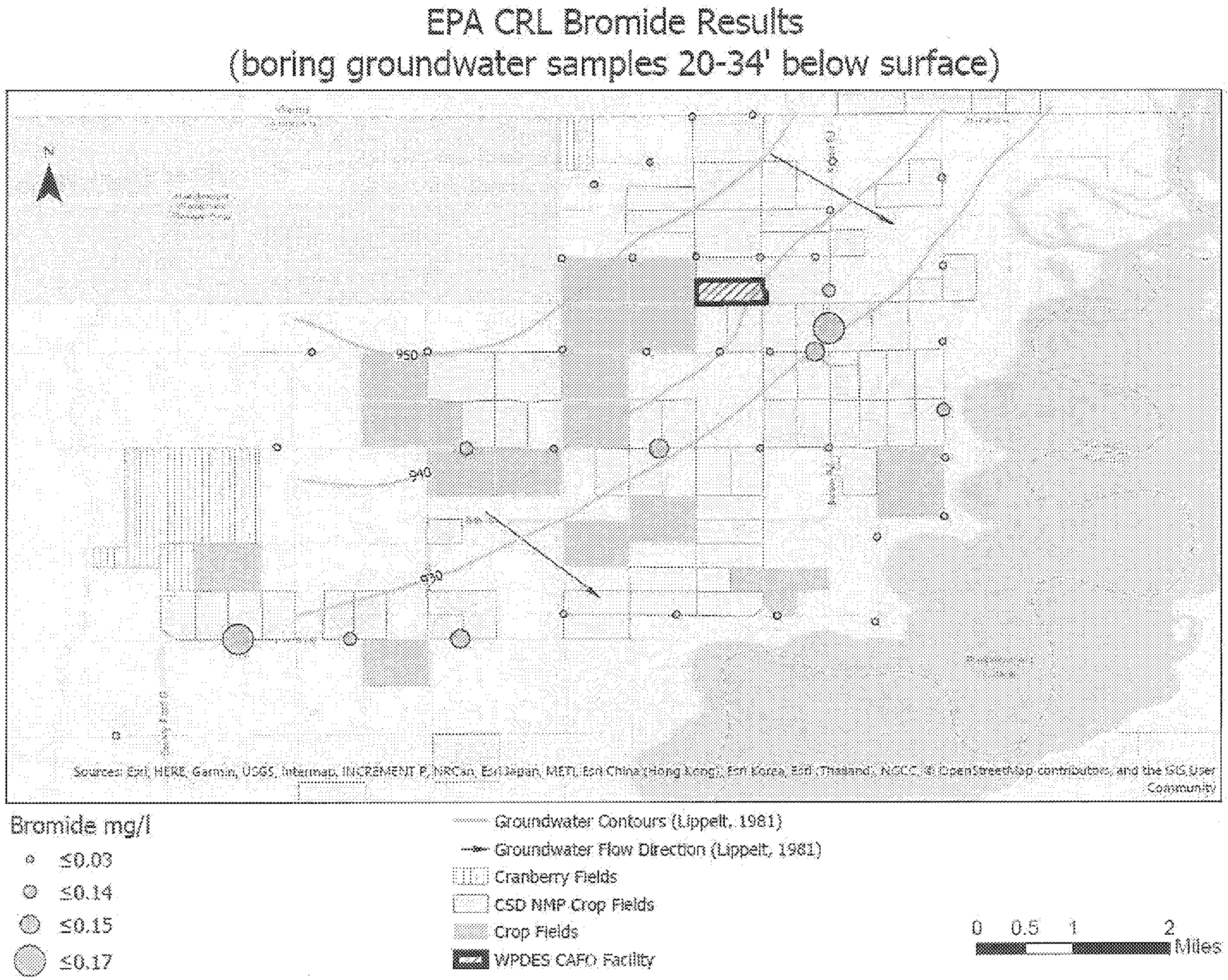
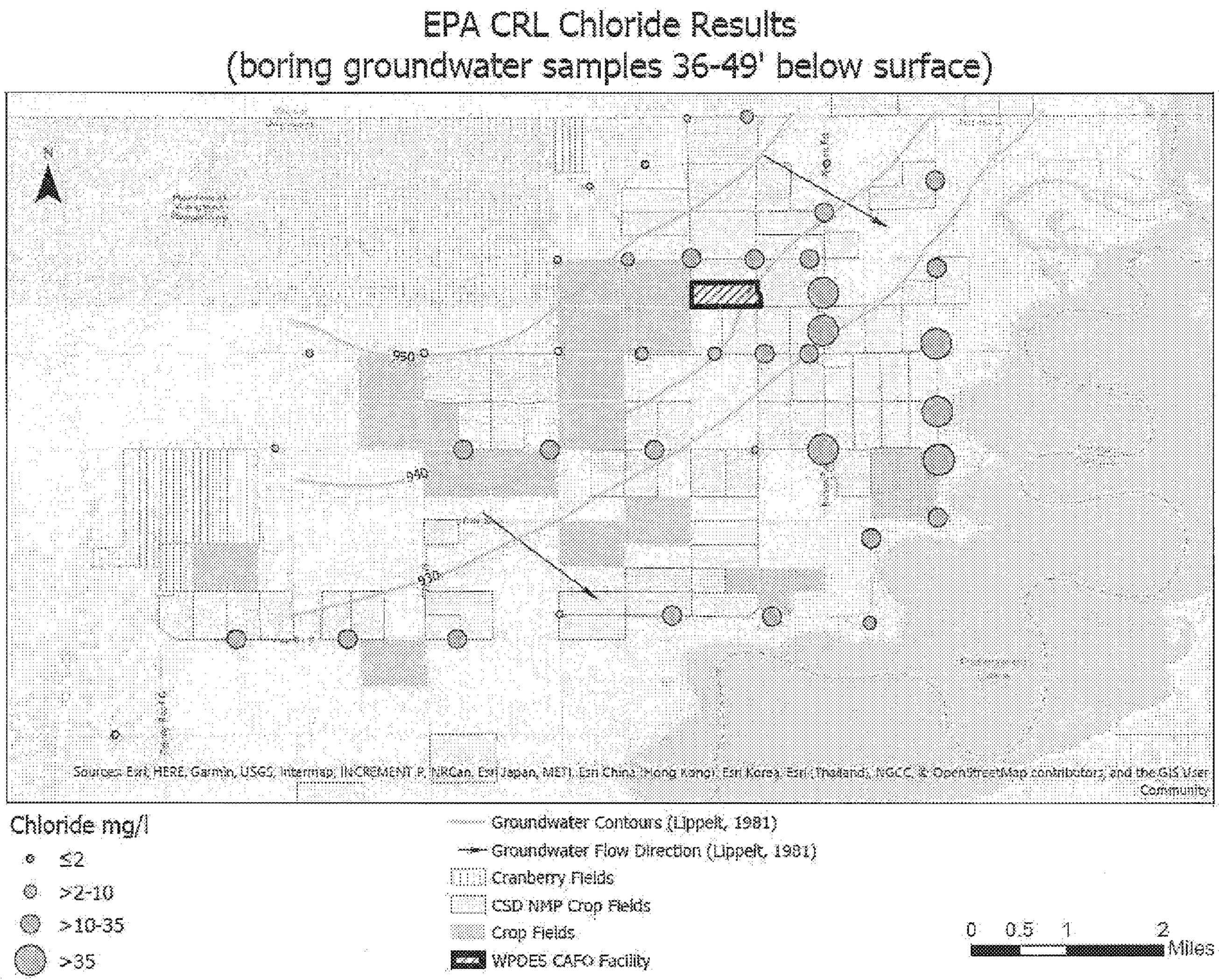
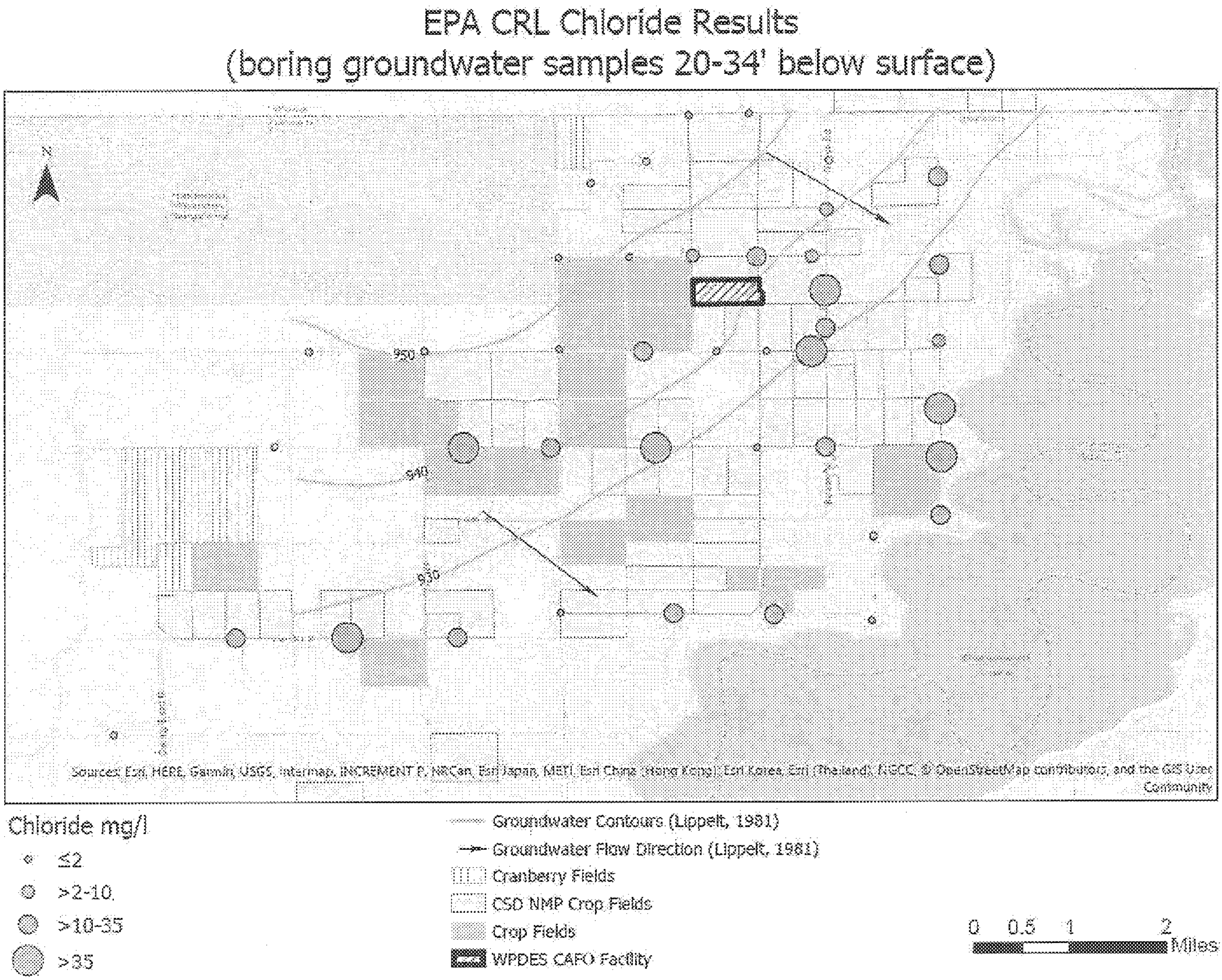

EPA CRL Bromide Results
(boring groundwater samples 20-34' below surface)
950
940
930
Sources: Esri, HERE, Garmin, USGS, Intermap, INCREMENT P, NRCan, Esri Japan, METI, Esri China (Hong Kong), Esri Korea, Esri (Thailand), NGCC, © OpenStreetMap contributors, and the GIS User Community
Bromide mg/l
≤0.03
≤0.14
≤0.15
≤0.17
Groundwater Contours (Lippelt, 1981)
Groundwater Flow Direction (Lippelt, 1981)
Cranberry Fields
CSD NMP Crop Fields
Crop Fields
WPDES CAFO Facility
0 0.5 1 2
Miles

Figure A-12.



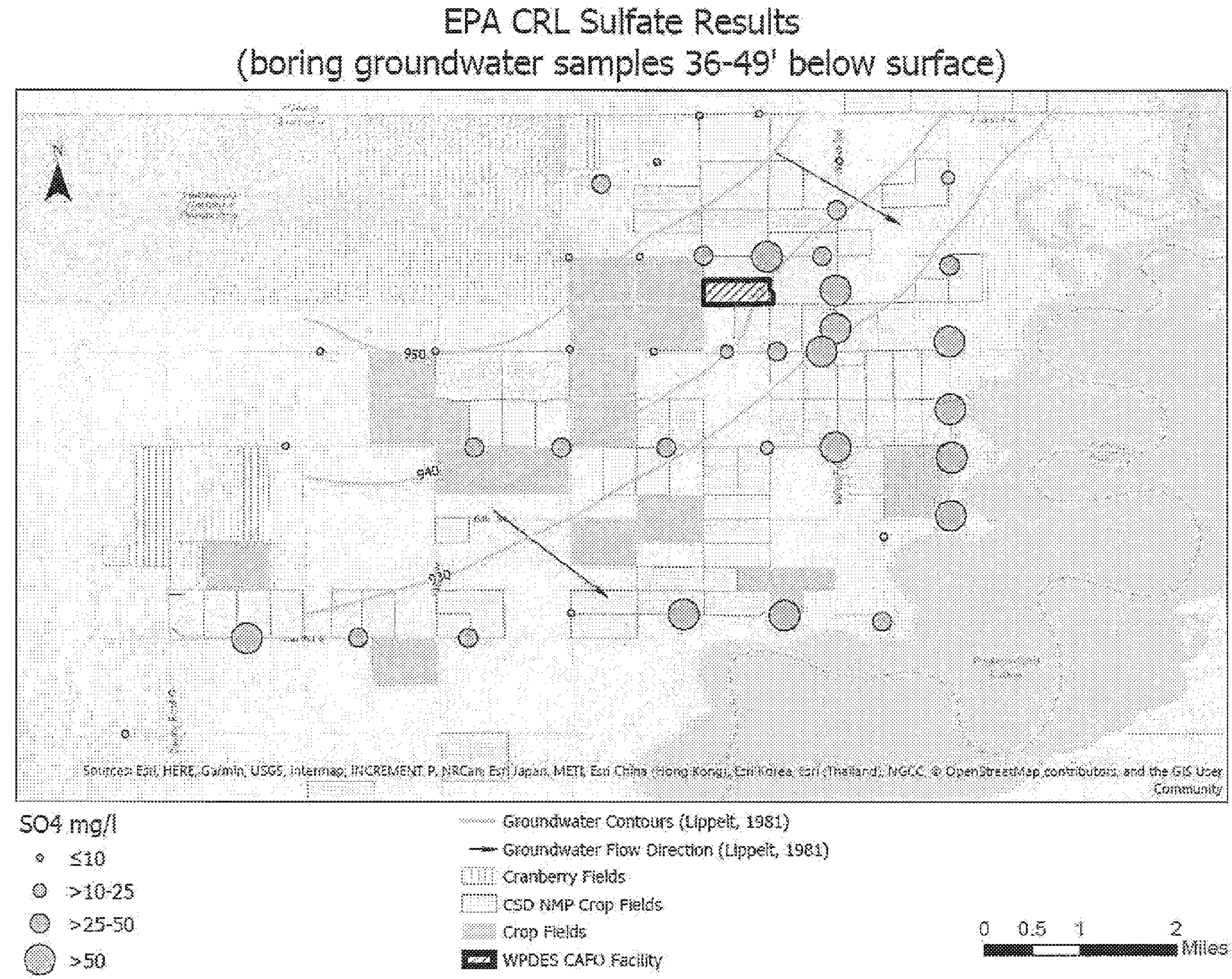
ED_004625A_00022255-00044

Figure A-13.



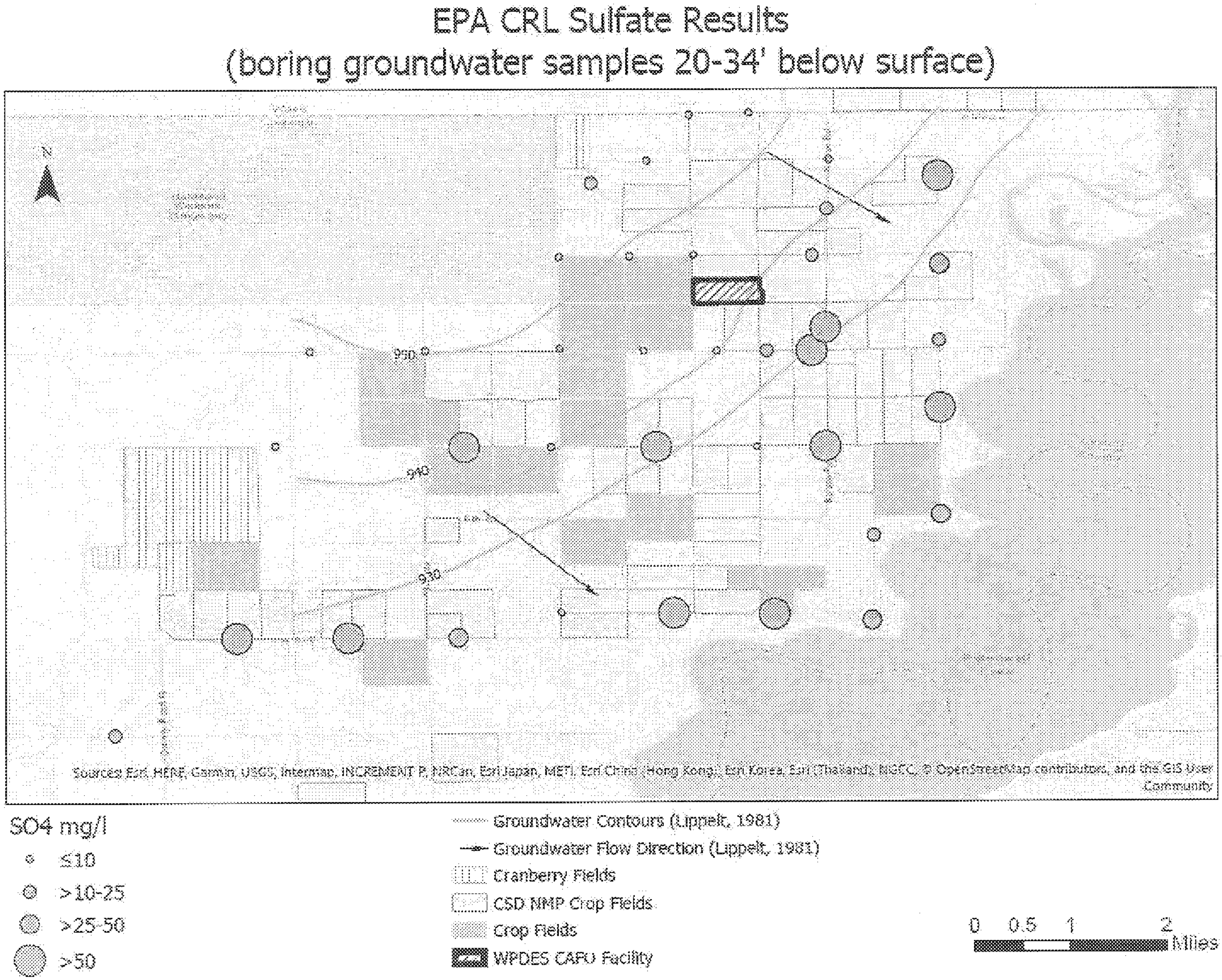
ED_004625A_00022255-00045

Figure A-14.



ED_004625A_00022255-00046

Figure A-15.



ED_004625A_00022255-00047

Figure A-16.

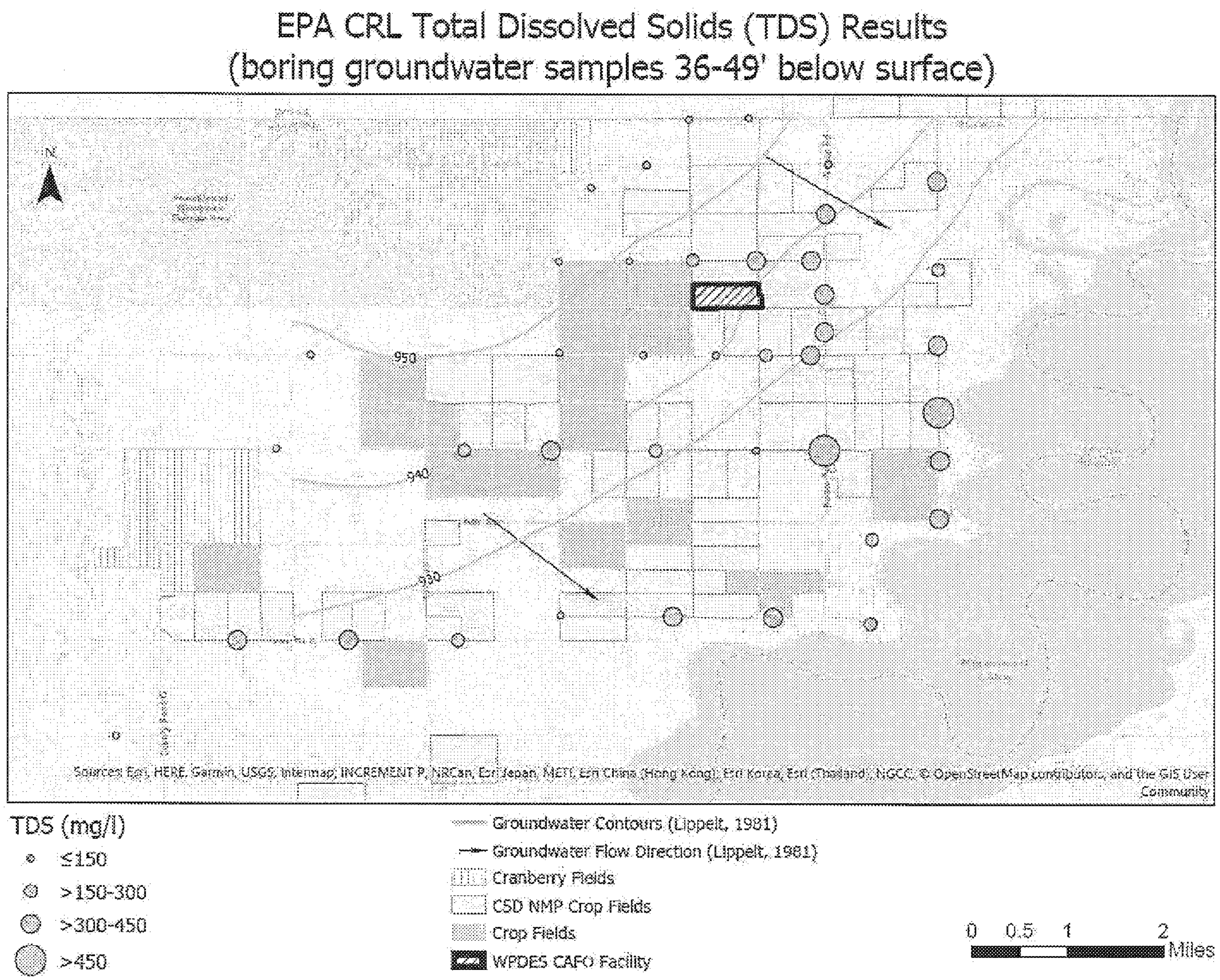
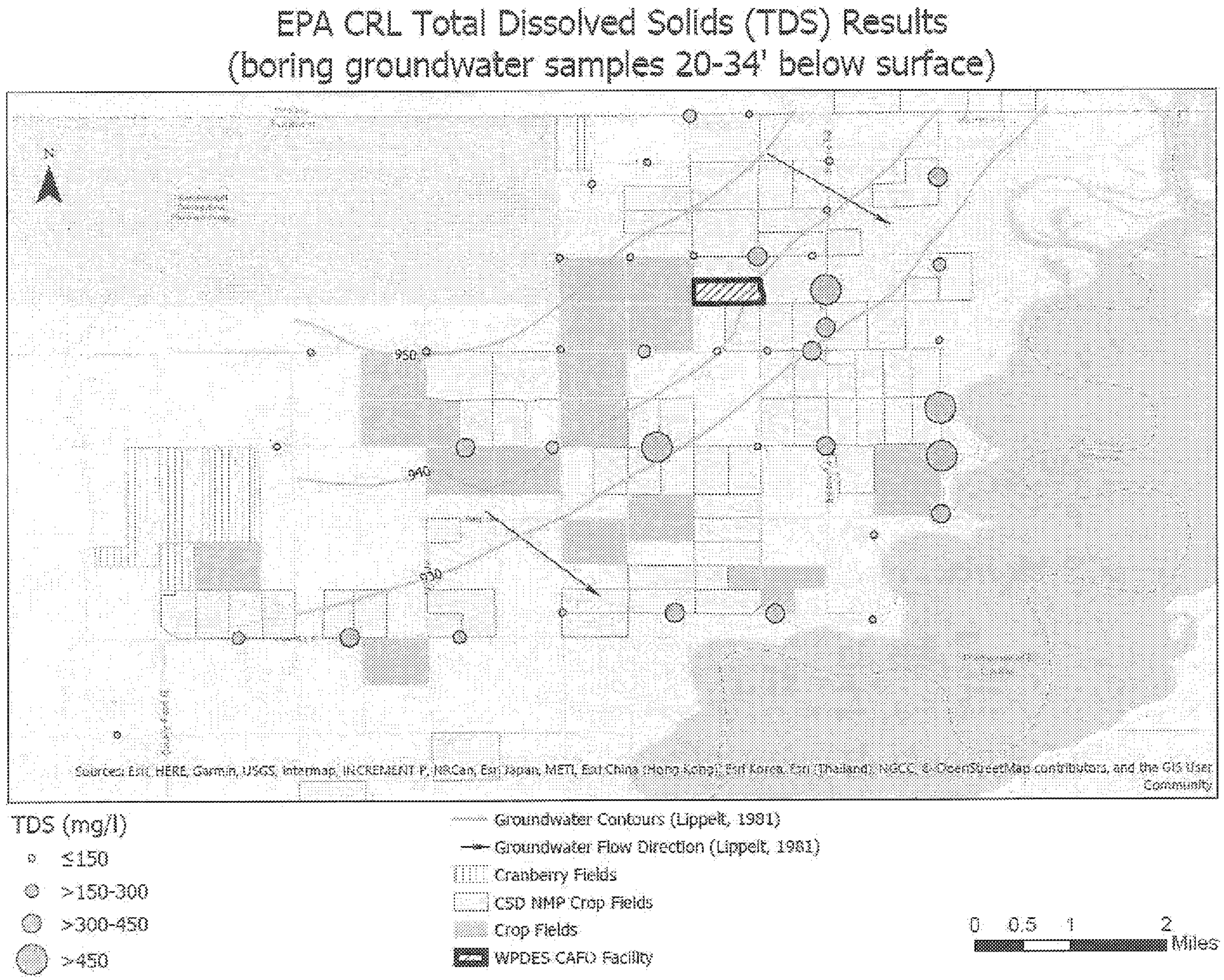
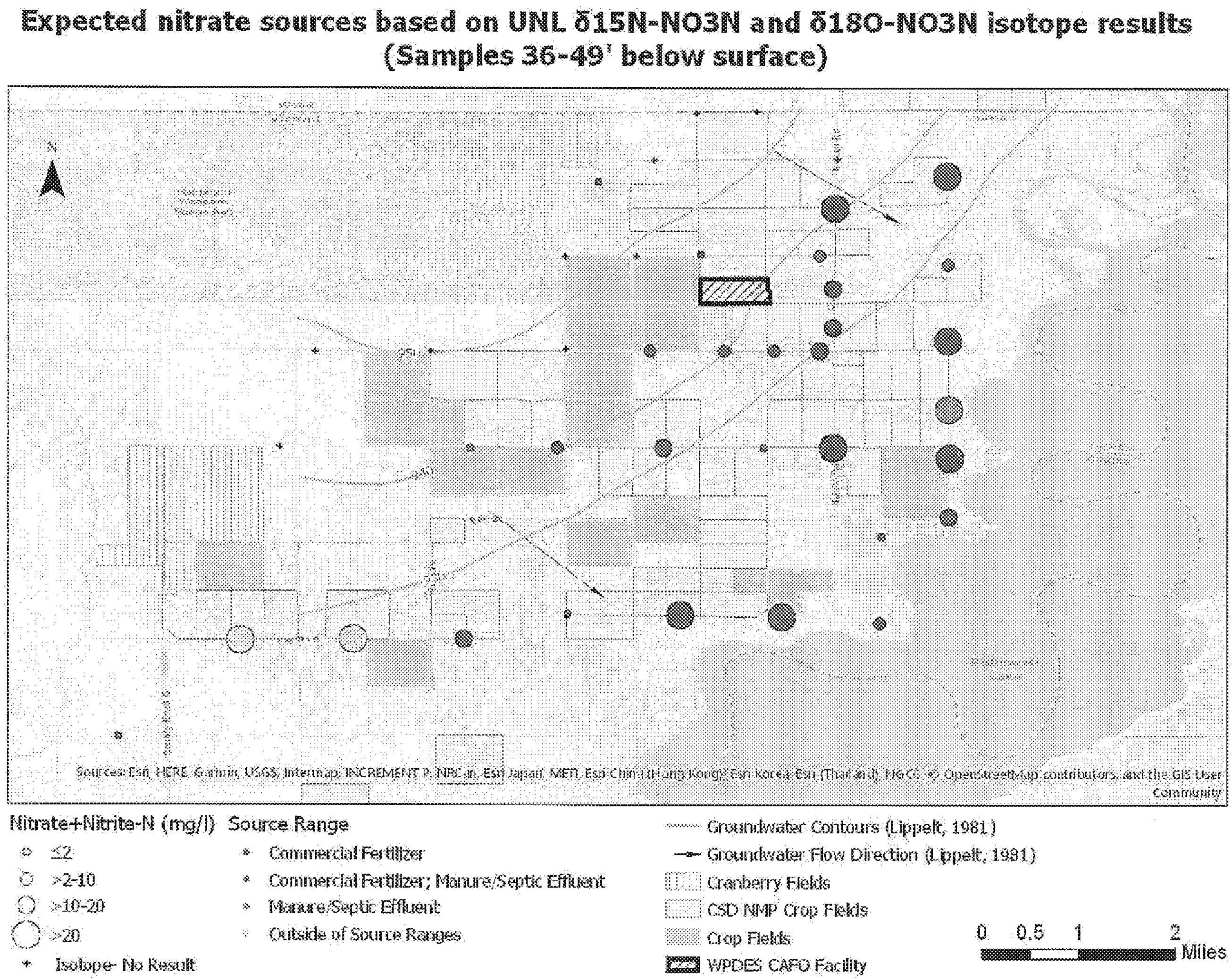

EPA CRL Total Dissolved Solids (TDS) Results
(boring groundwater samples 36-49' below surface)
950
940
930
Sources: Esri, HERE, Garmin, USGS, Intermap, INCREMENT P, NRCan, Esri Japan, METI, Esri China (Hong Kong), Esri Korea, Esri (Thailand), NGCC, © OpenStreetMap contributors, and the GIS User Community
TDS (mg/l)
≤150
>150-300
>300-450
>450
Groundwater Contours (Lippelt, 1981)
Groundwater Flow Direction (Lippelt, 1981)
Cranberry Fields
CSD NMP Crop Fields
Crop Fields
WPDES CAFO Facility
0 0.5 1 2 Miles

Figure A-17.



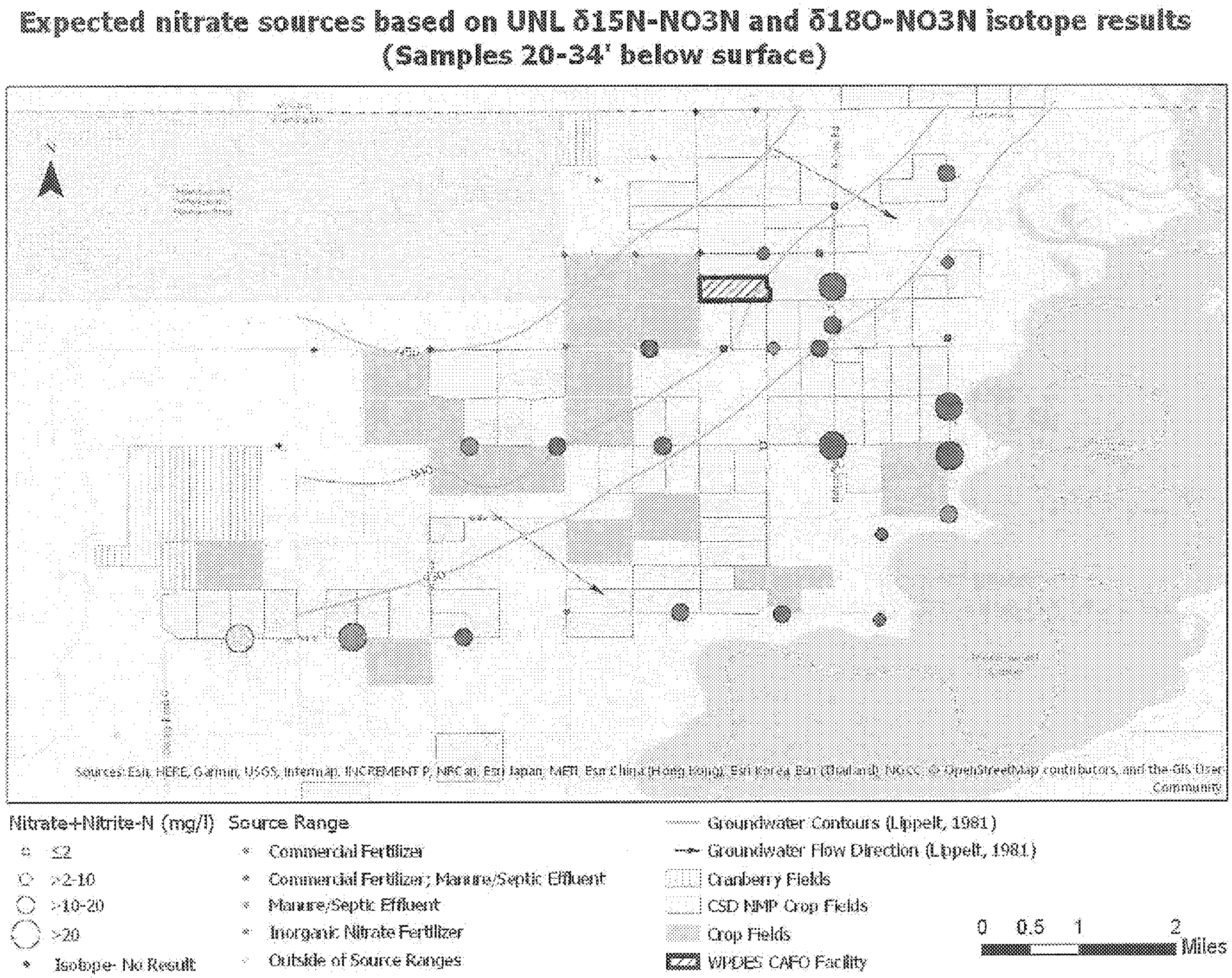
ED_004625A_00022255-00049

Figure A-18.



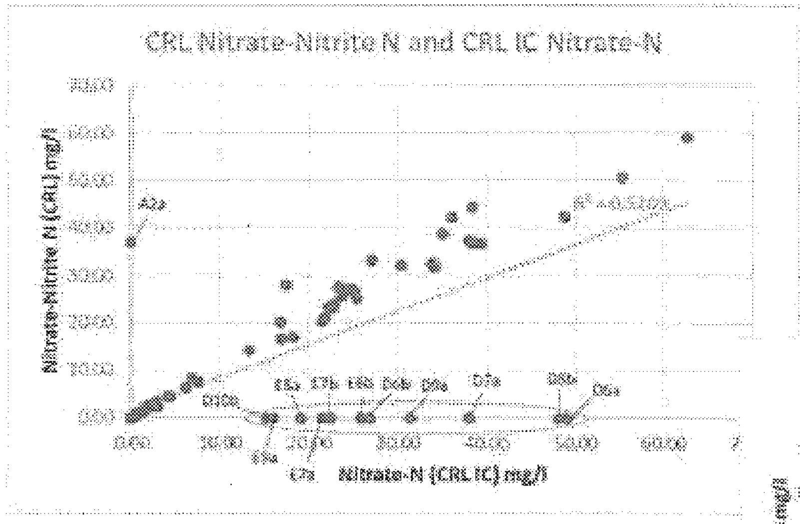
Expected nitrate sources based on UNL δ15N-NO3N and δ18O-NO3N isotope results
(Samples 36-49' below surface)
N
Sources: Esri, HERE, Garmin, USGS, Intermap, INCREMENT P, NRCan, Esri Japan, METI, Esri China (Hong Kong), Esri Korea, Esri (Thailand), NGCC, © OpenStreetMap contributors, and the GIS User Community
Nitrate+Nitrite-N (mg/l)
≤2
>2-10
>10-20
>20
Isotope- No Result
Source Range
Commercial Fertilizer
Commercial Fertilizer; Manure/Septic Effluent
Manure/Septic Effluent
Outside of Source Ranges
Groundwater Contours (Lippelt, 1981)
Groundwater Flow Direction (Lippelt, 1981)
Cranberry Fields
CSD NMP Crop Fields
Crop Fields
WPDES CAFO Facility
0 0.5 1 2
Miles

Figure A-19.



Expected nitrate sources based on UNL δ15N-NO3N and δ18O-NO3N isotope results
(Samples 20-34' below surface)
Sources: Esri, HERE, Garmin, USGS, Intermap, INCREMENT P, NRCan, Esri Japan, METI, Esri China (Hong Kong), Esri Korea, Esri (Thailand), NGCC, © OpenStreetMap contributors, and the GIS User Community
Nitrate+Nitrite-N (mg/l)
≤2
>2-10
>10-20
>20
Isotope- No Result
Source Range
Commercial Fertilizer
Commercial Fertilizer; Manure/Septic Effluent
Manure/Septic Effluent
Inorganic Nitrate Fertilizer
Outside of Source Ranges
Groundwater Contours (Lippelt, 1981)
Groundwater Flow Direction (Lippelt, 1981)
Cranberry Fields
CSD NMP Crop Fields
Crop Fields
WPDES CAFO Facility
0 0.5 1 2
Miles

Figure A-20. Comparison of Nitrate-Nitrite and CRL IC Nitrate-N with and without Inconsistent Data



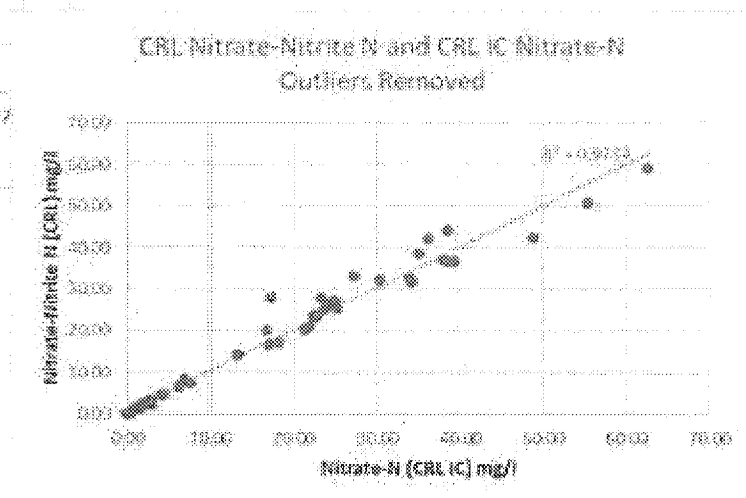
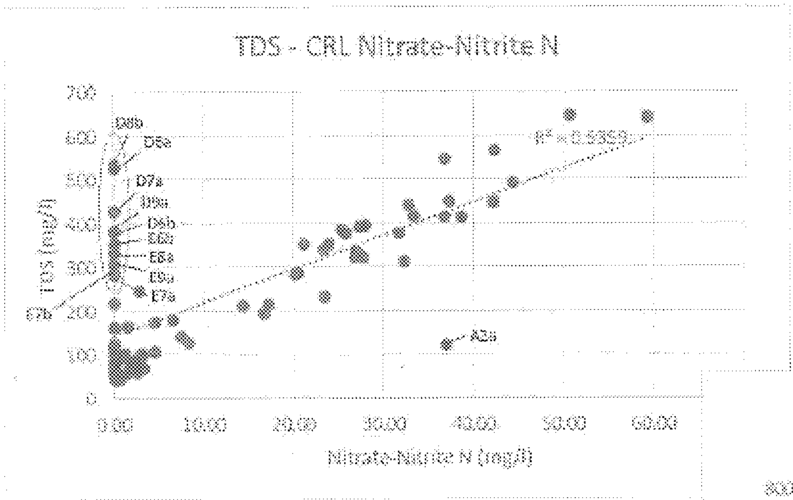
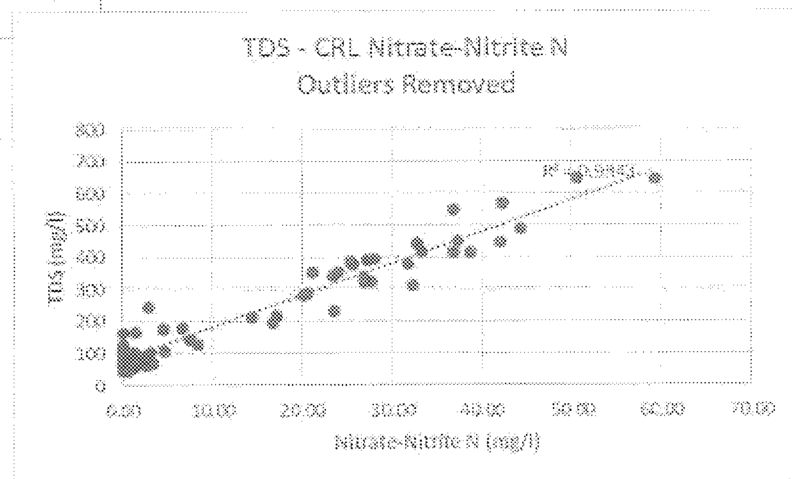


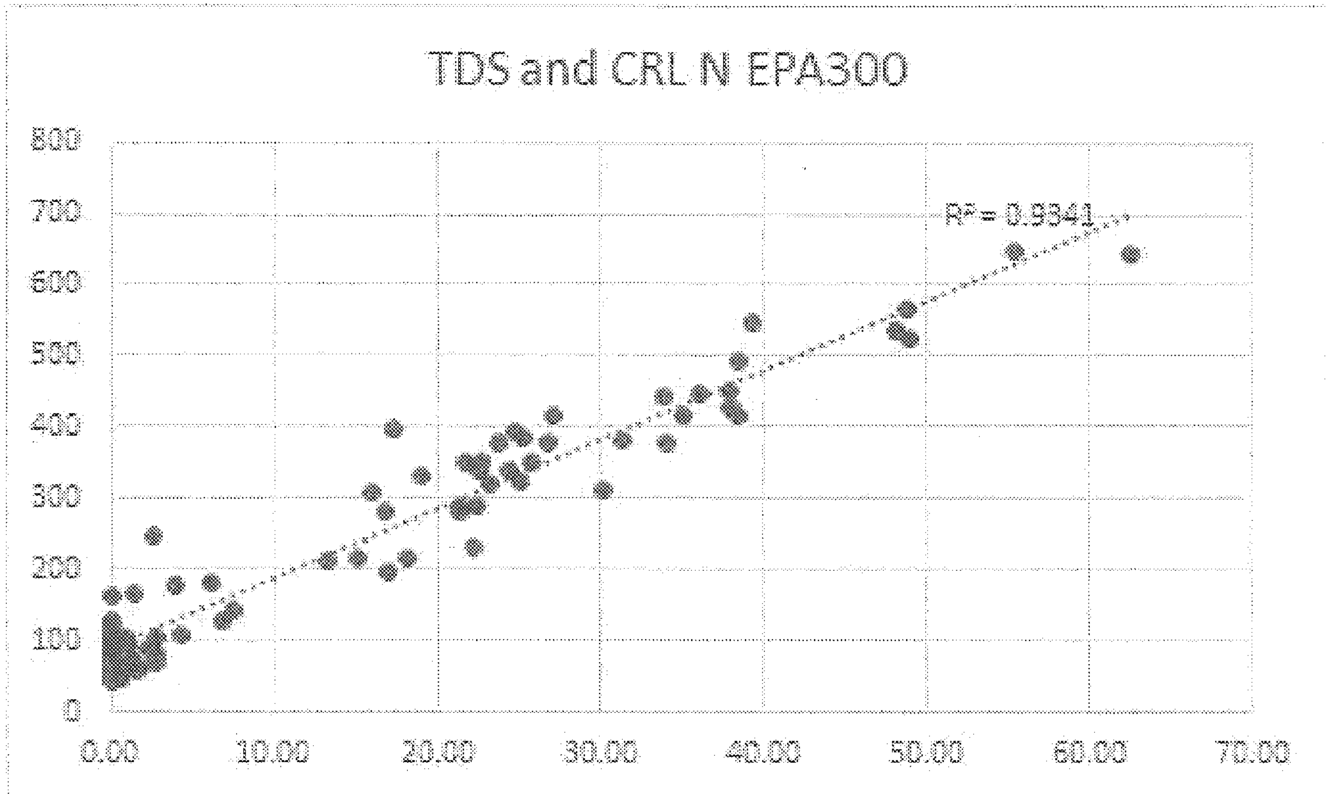
Figure A-21. TSD and CRL Nitrate-Nitrite N with and without Inconsistent Data





ED_004625A_00022255-00053

Figure A-22. TDS and CRL Nitrate-Nitrogen Method 300.0



APPENDIX B

Nitrate-N Isotope Results and Interpretation. Prepared for Eastern Research Group Prime Contract #EP-W-15-006. University of Nebraska Water Sciences Laboratory Lincoln, NE 68583-084, September 2018.

2018

Nitrate-N Isotope Results and Interpretation

Prepared for Eastern Research Group Prime Contract #EP-W-15-006

Daniel Snow, University of Nebraska Water Sciences Laboratory Lincoln, NE 68583-0844

Introduction

In May 2018, EPA conducted sampling at multiple locations in Wood and Juneau counties in Wisconsin up-gradient and down-gradient of Central Sands Dairy, LLC production area and land application fields. The purpose of the sampling was to identify potential manure contamination of ground water, surface water, and drinking water. EPA provided 87 samples to the University of Nebraska (UNL) Water Sciences Laboratory for $^{15}N\text{-}NO_3$ and $^{18}O\text{-}NO_3$ isotope analysis. UNL provided nitrate-N concentrations and stable isotope results for 71 of the 87 samples on June 11, 2018. EPA is requesting that UNL provide additional explanation and interpretation of the analytical results. This report will include the following:

- An explanation of the stable isotope analysis of nitrate, how it is measured, and how it may be applied in groundwater.
- A discussion of the expected ranges of nitrogen and oxygen isotope composition for nitrate due to sources and expected effects from denitrification using information from scientific literature.
- Plots of $^{15}N\text{-}NO_3$ versus nitrate concentration for samples received compared to expected ranges based on sources and effect from denitrification.
- Plots of measured $^{18}O\text{-}NO_3$ versus $^{15}N\text{-}NO_3$ compared to expected ranges based on sources and effect from denitrification.
- Evaluation of any anomalous results.
- Evaluation of isotope results in the context of other water chemistry data.
- List of supporting references

Background on stable isotope analysis of nitrate

Nitrate (NO_3) is composed of multiple stable isotopes of nitrogen and oxygen, and the composition or proportion of these isotopes changes in a predictable way in surface and groundwater systems. Moreover, nitrogen from specific sources has been shown to have a unique isotope composition or "fingerprint" which has led to a number of studies investigating the utility of linking nitrogen sources to nitrate contamination. The conventional method for measuring and reporting the stable isotope composition uses a delta (δ) notation based on the following equation:

$$\delta(o/oo) = \frac{R_{sample} - R_{air}}{R_{air}} \times 1000$$

where "R" is the measured isotope ratio of the less abundant isotope over the more abundant isotope for a sample and standard (air). In the case of nitrogen, "air" or atmospheric nitrogen gas is used as the reference standard with a very constant ^{15}N composition of 0.366% (Junk and Svec, 1958). The reference for oxygen isotopes is standard mean ocean water (SMOW) with a $^{18}O/^{16}O$ = 2005.2 ppm.

Measurement of Nitrate Isotopes

A number of methods for high precision stable isotope analysis of nitrate have been published over the past several decades. A recent mini-review discusses advantages and disadvantages of the most common approaches (Dai, Xie, et al., 2017). All methods require separation and conversion of dissolved nitrate into gases that can be introduced into a high precision light gas stable isotope mass spectrometer. Early methods, such as those published by (Spalding, Gormly, et al., 1978) and used at the Water Sciences Laboratory until 2017, required multiple chemical conversions, labor-intensive steam distillation and high vacuum gas-phase oxidation to purified nitrogen (N_2) gas. While a proven technique, most analytical approaches use either ion exchange separation of nitrate, followed by high temperature conversion to nitrogen gas and carbon monoxide using an elemental analyzer ((Silva, Kendall, et al., 2000), or direct chemical (McIlvin and Altabet, 2005) or microbial (Casciotti, Sigman, et al., 2002) conversion to nitrous oxide (N_2O). The newer methods are faster, can be semi-automated and permit direct measurement of both nitrogen and oxygen isotopes in nitrate.

The method employed at the Water Sciences Laboratory uses a two-step chemical conversion of nitrate using alkaline Cd-reduction of dissolved nitrate to nitrite, followed by acidic reaction of nitrite with azide to produce nitrous oxide (N_2O). N_2O is purged and cryogenically trapped on an Isoprime Tracegas preconcentrator interfaced with a GVI isotope ratio mass spectrometer. Trapped N_2O is chromatographically separated from nitrogen gas, and ions with m/z =44, 45, and 46 are simultaneously separate and monitored on a multi-collector magnetic sector mass spectrometer. Standard nitrate solutions of from known, or isotopically-characterized nitrate are processed and analyzed in the same way as samples, and the results used for calibrating the mass spectrometer and determining. A working N_2O gas standard is measured between every sample and the ratios 44/45 and 44/46 converted to deltas (δ) using the instrument software.

Stable Isotope "Fingerprinting" of Nitrate

Nitrogen in commercial fertilizers (urea and anhydrous ammonia) has an isotope composition very similar to atmospheric nitrogen, and typically ranges from -6 to +6 per mil (‰)(Kendall, Elliott, et al., 2008). Extensive data collection and analysis of fertilizer sources has suggested that the isotope composition of the majority (~80%) of inorganic nitrogen fertilizer sources ranges between -3 and +3‰ (Michalski, Kolanowski, et al., 2015). In comparison, nitrogen from animal manure, sewage or biosolids tends to be enriched in the heavier ^{15}N isotope, especially after deposition and conversion to the highly volatile ammonia (Kendall, Elliott et al. 2008), and its range tends to be significantly higher, typically between +10 and +25‰. Oxygen isotopes in nitrate, may either originate from the oxygen in a commercial nitrate fertilizer (KNO_3 or $N_2H_4O_3$) or from oxygen atoms in the soil, air, and water during nitrification of ammonia. Because the oxygen isotope composition in air is relatively constant (+22 to +24‰), and the oxygen isotope composition of water changes in a predictable way (usually -5 to -20‰), it is possible to predict the oxygen isotope composition of soil nitrate formed by nitrification.

Both the nitrogen and oxygen isotope composition can be changed in nitrate by another process called microbial denitrification, changes nitrate to nitrite, nitrous oxide, and may eventually convert nitrate to nitrogen gas and water. Because the change in composition is predictable, simultaneous measurement of both nitrogen and oxygen isotopes can provide clues about the source(s) of nitrogen, timing of nitrification (nitrate formation), and whether denitrification has helped to remove any nitrate. As figure 1 indicates, however, the use of both nitrogen and oxygen isotopes for distinguishing sources of nitrate in groundwater can be complicated by multiple sources (atmospheric, manure, septic systems) and processes.

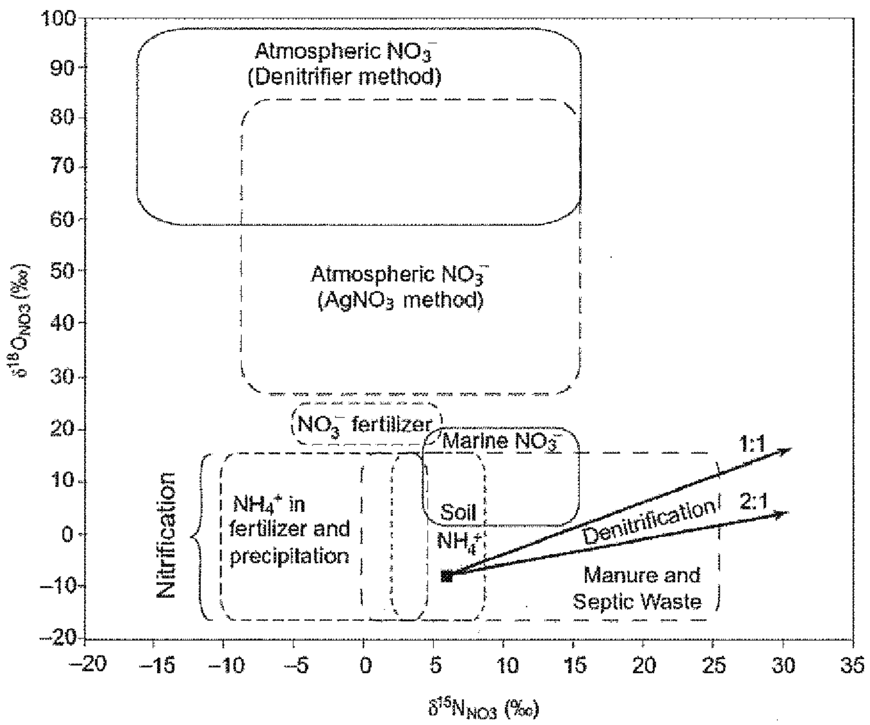


Figure 1. Expected variation of ^{15}N-NO_3 and ^{18}O-NO_3 from a variety of sources, along with the predicted trends due to denitrification (Kendall et al 2008).

Finally, interpretation of the measured isotope composition of nitrate in groundwater samples with respect to potential sources should include consideration of the expected ranges from sources, potential for mixing multiple nitrogen sources, and the possibility of changes in the isotope composition due to biogeochemical processes (Kendall and Aravena, 2000). While this is often challenging, comparing the measured isotope composition of nitrate with other parameters, such as dissolved oxygen, iron, chloride and alkalinity, can help support interpretations.

Trends from the Study Area Samples

Figure 2 shows the relationship between increasing isotope composition with groundwater nitrate concentrations of samples analyzed for this study. Denitrification of a single (organic or inorganic fertilizer) source can be indicated by an inverse trend between groundwater nitrate-N concentration and nitrogen-15 content of residual nitrate (Gormly and Spalding, 1979), especially with increasing depth. A single source of nitrogen is not indicated by the relationship between nitrate concentration and $\delta^{15}N$-NO_3.

Plots of the $\delta^{15}N$-NO_3N composition versus the natural log and inverse ($1/NO_3N$) concentrations can help distinguish between denitrification and simple mixing. Figure 3 shows the relationship between the natural log of nitrate-N concentrations (mg/L) versus $\delta^{15}N$-NO_3N composition of nitration. A log-linear trend between nitrate-N concentration and $\delta^{15}N$-NO_3N provides evidence supporting microbial denitrification as a factor controlling the isotope composition of groundwater nitrate (Kendall and Aravena, 2000). As noted above, biogeochemical transformation of nitrate can increase the nitrate-N isotope composition and must be considered when interpreting nitrate isotope results. The correlation is weak, however, suggesting denitrification is not the only process contributing to enrichment of $\delta^{15}N$-NO_3N.

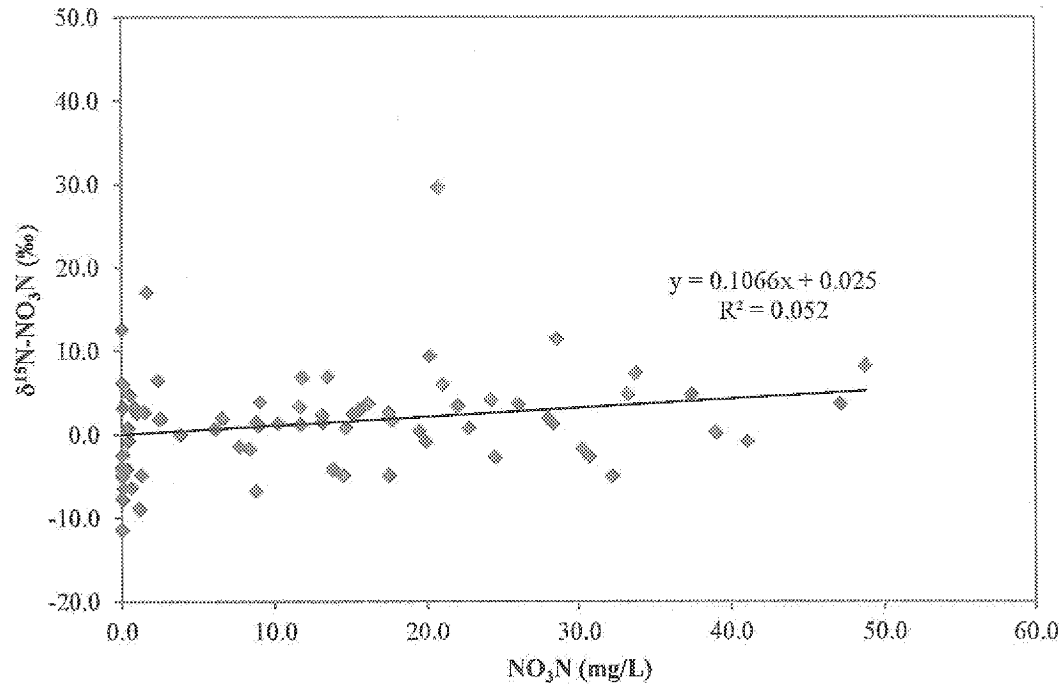


Figure 2. Correlation between $\delta^{15}N$-NO_3N and groundwater nitrate concentrations. Trend line is consistent with an overall increase of nitrogen-15 isotope composition with increasing concentration.

A plot of $\delta^{15}N$-NO_3N versus $\delta^{18}O$-NO_3N is shown in figure 5 together with expected ranges for nitrate resulting from nitrified commercial nitrogen fertilizer (anhydrous ammonia, urea, etc.), nitrate-N from manure and septic system effluent, and inorganic nitrate fertilizer sources. Only 1 sample plots in the isotope range inorganic nitrate fertilizers, while over 50% of the samples plot in the range expected for nitrification of commercial nitrogen fertilizer. Roughly one-third of the isotope results fall in the range expected for manure and septic system nitrogen, and several points are consistent with enrichment due to denitrification (Kendall, Elliott, et al., 2008).

Unusual or Anomalous Isotope Results

The majority of the nitrate isotope composition measured are consistent with ranges expected from nitrification of commercial nitrogen fertilizer or organic nitrogen sources. Denitrification of nitrate-N in the groundwater would be expected to shift both the $\delta^{15}N$-NO_3N and $\delta^{18}O$-NO_3N to more enriched values and several points are consistent with this enrichment. Samples from location "E" tend to have isotopically enriched nitrate, and also are lower in dissolved chloride and sulfate (Table 1). Nitrate from sample ID "E9a" (45' depth) had the highest measured $\delta^{15}N$-NO_3 = +29.79‰ and is consistent with nitrogen from an organic source. Several samples had very low (negative) $\delta^{15}N$-NO_3N results, ranging from -5 to -11.41‰. Negative, or depleted δ15N-NO3N occurs during incomplete nitrification of soil nitrification. Significant depletion of

$\delta^{15}N\text{-}NO_3N$ can also occur during partial denitrification (Bates, Martin, et al., 1998, Kendall, Elliott, et al., 2008).

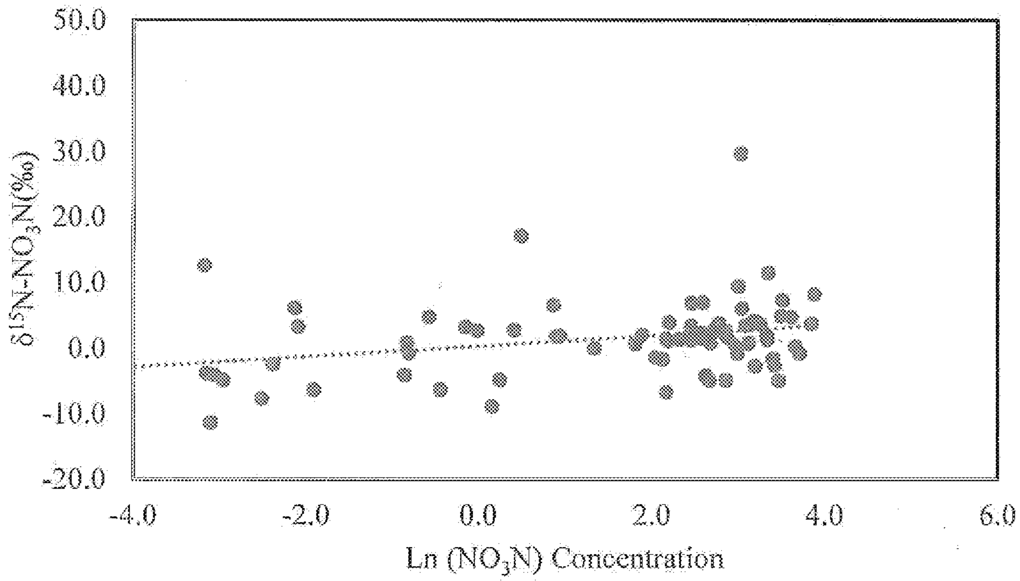


Figure 3. Trend of the natural log (Ln) of nitrate-N concentrations versus $^{15}N\text{-}NO_3$ composition of nitrate. A linear trend is consistent with microbial fraction due to denitrification.

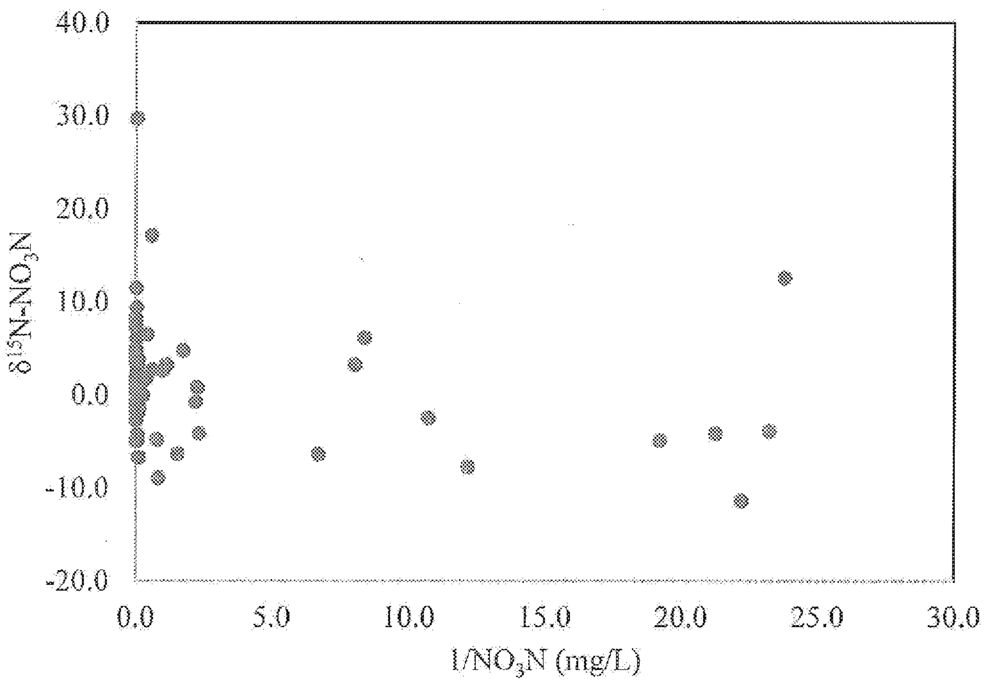


Figure 4. Trend of inverse nitrate concentration (1/NO3N) versus $^{15}N\text{-}NO_3N$ of nitrate. Simple mixing or dilution of a single source would be indicated by a linear correlation.

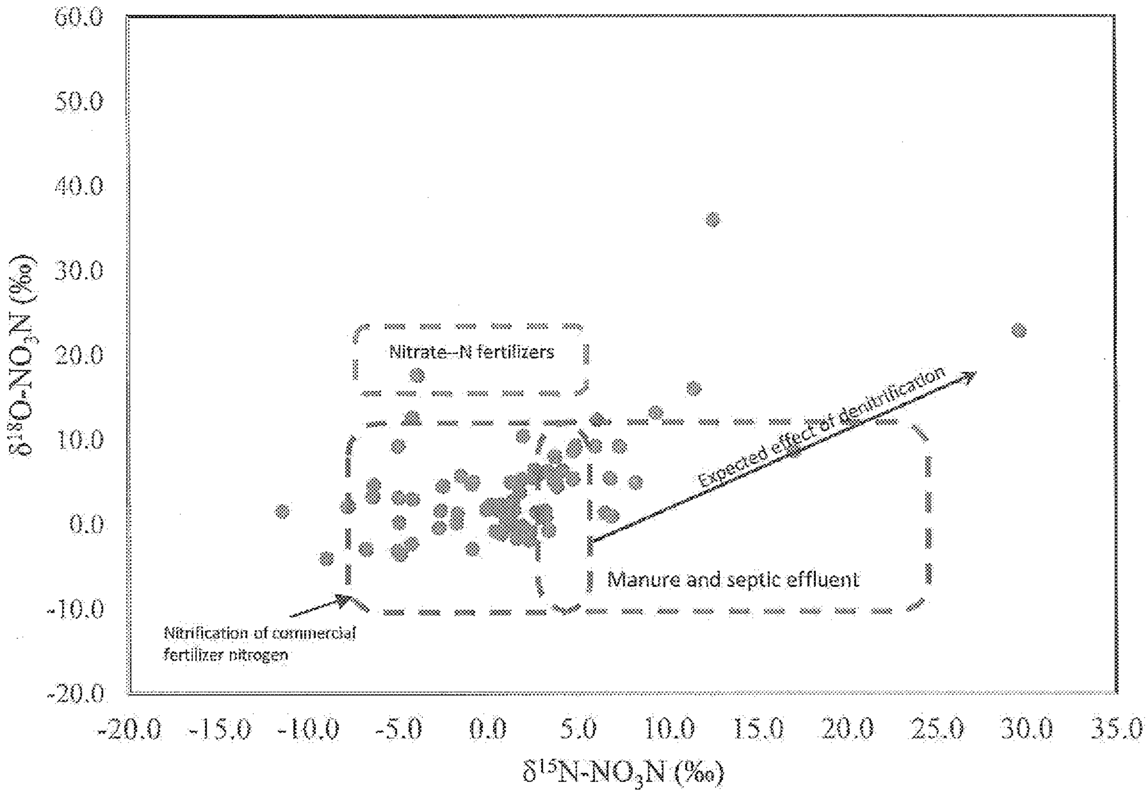


Figure 5. Measured $\delta^{15}N$-NO_3N versus $\delta^{18}O$-NO_3N compared to expected ranges from commercial fertilizer sources (dark blue dashed box), manure and septic sources (orange dashed box) and inorganic nitrate fertilizers (green box). Trend arrow of increasing $\delta^{18}O$-NO_3N and $\delta^{15}N$-NO_3N for enrichment due to denitrification. Ranges and arrow from (Kendall and Aravena, 2000).

Related Water Chemistry

A spreadsheet listing of related water chemistry data collected with these samples was received July 26th from Cheryl Burdett, including samples analyzed at EPA's Chicago Regional Laboratory. Selected results are included in Table 1 for direct comparison of nitrate isotope measurements with field measurements (pH, temperature, depth), nitrate-N concentrations, δ^{15}N-NO$_3$N, δ^{18}O-NO$_3$N, dissolved chloride, sulfate, ammonia-N, iron and manganese. Nitrate-N concentrations from field samples averaged 10.0±11.6, and concentrations higher than 10 tended to occur in deeper samples (>30') and in samples collected toward the end of the sampling event. Samples with higher nitrate concentration also tended to have elevated chloride, sulfate, ammonia-N and iron (Table 1). Elevated iron and ammonia-N concentrations are consistent with reducing conditions in groundwater likely to encourage microbial denitrification. Total organic carbon was measured but did not appear to show any trend with other parameters. There is a general positive correlation (R^2=0.67 of dissolved chloride with sulfate, and samples with high dissolved chloride tend to have lower δ^{15}-NO$_3$N characteristic of commercial nitrogen sources.

Literature Cited

Junk, G. and H.J. Svec. 1958. The absolute abundance of the nitrogen isotopes in the atmosphere and compressed gas from various sources. Geochim. Cosmochim. Acta 14: 234-243.

Kendall, C. and R. Aravena. 2000. Nitrate Isotopes in Groundwater Systems. In: P. G. Cook and A. L. Herczeg, editors, Environmental Tracers in Subsurface Hydrology. Springer US, Boston, MA. p. 261-297.

Kendall, C., E.M. Elliott and S.D. Wankel. 2008. Tracing Anthropogenic Inputs of Nitrogen to Ecosystems. Stable Isotopes in Ecology and Environmental Science. Blackwell Publishing Ltd. p. 375-449.

Michalski, G., M. Kolanowski and K.M. Riha. 2015. Oxygen and nitrogen isotopic composition of nitrate in commercial fertilizers, nitric acid, and reagent salts. Isotopes in Environmental and Health Studies 51: 382-391. doi:10.1080/10256016.2015.1054821.

Table 1. Summary of field parameter data, nitrate and nitrate isotope measurements, together with selected water chemistry data from EPA's Chicago Regional Laboratory.

Field Measurements						**University of Nebraska**					**EPA R5 Laboratory**					
Sample_ID	SampleDate_Time	pH_SU	Water_Temperature_C	Nitrate_Field_Test_mgl	Sample_Depth_from_Surface_ft	Sample_ID	NO3+NO2-N	Sample_ID	15N-NO3	18O-NO3	Sample ID	Chloride (mg/L)	Sulfate (mg/L)	Ammonia-N (mg/L)	Iron (ug/l)	Manganese (ug/l)
A1a	4/30/18 7:19	7.9	11.6	5	45	A1A	0.000	A1A	--	--	A1a	4.6	7.0	0.25	115.0	2.1
A2a	4/30/18 8:15	7.31	11.1	0	45	A2A	0.000	A2A	--	--	A1b	1.2	6.0	0.36	43.1	1.0
A2b	4/30/18 8:24	7.38	10.4	1	24	A2B	0.006	A2B	--	--	A2a	1.2	9.8	0.31	98.4	2.3
A3a	4/30/18 9:06	7.76	13	1	45	A3A	0.021	A3A	--	--	A2b	0.9	5.0	0.29	30.7	3.0
A3b	4/30/18 9:14	6.65	12.5	0	20	A3B	0.047	A3B	-4.15	12.52	A3a	0.8	8.8	U	51.6	2.3
A4a	4/30/18 9:58	6.55	12.8	2	45	A4A	0.568	A4A	4.76	5.27	A3b	0.8	6.4	U	81.4	2.5
A4b	4/30/18 10:09	6.09	12.2	4	20	A4B	0.124	A4B	3.23	0.70	A4a	1.0	26.5	U	38.3	0.8
B1a	4/30/18 10:51	7.04	13.2	0	45	B1A	0.018	B1A	--	--	A4b	0.5	10.7	0.25	30.7	1.5
B1b	4/30/18 10:58	6.57	12.5	0	20	B1B	0.043	B1B	-3.89	17.57	B1a	0.7	8.2	0.25	31.2	1.0
B2a	4/30/18 11:40	7.38	12	0	45	B2A	0.000	B2A	--	--	B1b	1.1	7.9	0.21	88.9	0.9
B2b	4/30/18 11:48	6.38	11.5	0	20	B2B	0.082	B2B	-7.73	2.04	B2a	2.8	8.8	U	82.4	1.6
B3a	4/30/18 12:29	6.42	13.4	5	45	B3A	1.284	B3A	-4.83	-3.64	B2b	0.5	5.1	U	39.1	0.6
B3b	4/30/18 12:36	6.25	12.5	2	20	B3B	0.000	B3B	--	--	B3a	19.5	26.3	0.62	35.0	3.6
B4a	4/30/18 13:10	6.77	15.5	50	45	B4A	17.473	B4A	-4.91	0.17	B3b	2.1	6.7	0.37	87.1	2.2
B4b	4/30/18 13:41	6.47	14.7	50	20	B4B	8.807	B4B	1.41	2.66	B4a	35.0	66.3	0.61	19.0	4.0
C3a	4/30/18 14:16	6.32	16.5	20	45	C3A	9.083	C3A	3.88	4.41	B4b	26.7	112.0	3.56	93.4	1.8
C3b	4/30/18 14:26	6.16	16.5	3	20	C3B	0.440	C3B	0.81	-1.22	C1a	0.7	7.8	U	14.0	1.2

Field Measurements						University of Nebraska					EPA R5 Laboratory					
Sample_ID	SampleDate_Time	pH_SU	Water_Temperature_C	Nitrate_Field_Test_mgl	Sample_Depth_from_Surface_ft	Sample_ID	NO3+NO2-N	Sample_ID	15N-NO3	18O-NO3	Sample ID	Chloride (mg/L)	Sulfate (mg/L)	Ammonia-N (mg/L)	Iron (ug/l)	Manganese (ug/l)
C1a	4/30/18 15:02	6.25	14.6	0	45	C1A	0.000	C1A	--	--	C1b	0.7	6.5	U	13.4	1.9
C1b	4/30/18 15:27	6.58	14.8	0	30	C1B	0.045	C1B	-11.41	1.50	C2a	34.4	29.2	0.25	12.9	4.0
C2a	4/30/18 16:06	6.05	15.6	50	45	C2A	22.807	C2A	0.75	2.30	C2b	3.3	15.7	0.81	53.9	9.5
A1b	4/30/18 7:32	6.9	9.8	3	20	A1B	0.052	A1B	-4.94	9.19	C3a	30.0	40.9	1.19	31.9	14.3
C2b	4/30/18 16:14	6.46	16.5	10	30	C2B	0.866	C2B	3.22	1.51	C3b	5.8	11.5	0.24	6.8	0.8
C5Aa	5/1/18 6:29	6.11	12.2	20	45	C5AA	13.147	C5AA	2.32	-1.91	C5Aa	38.8	90.4	0.6	15.9	3.9
C5Ab	5/1/18 6:43	6.64	12.1	50	30	C5AB	22.042	C5AB	3.42	-0.80	C5Ab	50.5	101.0	2.13	126.0	8.1
C6a	5/1/18 7:06	8.35	11.8	50	45	C6A	15.132	C6A	2.40	-0.95	C6a	43.5	54.7	0.71	21.1	9.6
C6b	5/1/18 7:15	6.8	12	50	30	C6B	11.703	C6B	1.19	0.79	C6b	29.5	88.9	3.96	54.8	10.7
C7a	5/1/18 7:48	8.28	14.2	50	45	C7A	19.503	C7A	0.45	-0.85	C7a	33.6	52.5	U	19.6	9.9
C7b	5/1/18 8:02	6.3	13.1	50	30	C7B	14.692	C7B	0.78	2.17	C7b	35.9	95.2	0.27	91.4	11.6
C8a	5/1/18 8:35	6.44	13.1	20	45	C8A	6.636	C8A	1.99	10.37	C8a	15.9	44.5	0.25	18.9	12.2
C8b	5/1/18 8:42	6.48	13.5	5	30	C8B	2.392	C8B	6.53	1.34	C8b	1.8	15.9	0.26	24.4	3.7
C9a	5/1/18 10:00	6.1	15.9	2	45	C9A	2.470	C9A	1.81	3.76	C9a	3.7	16.4	0.2	73.1	3.5
C9b	5/1/18 10:21	6.03	12.7	2	30	C9B	0.646	C9B	-6.33	4.59	C9b	0.6	6.7	0.2	10.6	2.1
C10a	5/1/18 11:05	6.8	12.6	5	45	C10A	7.760	C10A	-1.46	5.69	C10a	6.9	3.4	0.76	9.5	3.2
C10b	5/1/18 11:12	6.63	12.4	20	30	C10B	15.606	C10B	3.03	5.99	C10b	31.3	2.0	3.91	83.8	3.8
C11a	5/1/18 11:46	6.93	14.6	0	45	C11A	0.000	C11A	--	--	C11a	0.8	9.0	0.41	40.2	1.6
C11b	5/1/18 11:52	6.75	13.9	1	30	C11B	0.119	C11B	6.10	12.32	C11b	0.9	6.7	1.08	61.7	2.4
C12a	5/1/18 12:41	6.8	14.1	0	32	C12A	0.000	C12A	--	--	C12a	1.7	0.9	1.22	130.0	1.8
C12b	5/1/18 12:47	7.08	13.5	0	20	C12B	0.000	C12B	--	--	C12b	1.3	0.9	1.51	154.0	12.8
C13a	5/1/18 13:30	6.7	13.7	0	45	C13A	0.000	C13A	--	--	C13a	0.6	6.5	0.26	43.4	0.9
C13b	5/1/18 13:39	7.12	13	0	30	C13B	0.000	C13B	--	--	C13b	1.3	7.3	1.32	130.0	1.1
D1a	5/1/18 14:19	7.03	14	0	45	D1A	0.000	D1A	--	--	D1a	0.5	7.7	0.26	39.2	2.0
D1b	5/1/18 14:26	6.83	15.5	0	30	D1B	0.000	D1B	--	--	D1b	0.8	4.9	0.68	70.5	0.6
D2a	5/1/18 15:00	7.56	14.3	5	45	D2A	1.652	D2A	17.09	8.63	D2a	17.3	44.3	U	26.6	1.2
D2b	5/1/18 15:06	6.47	14.1	50	30	D2B	13.455	D2B	6.94	0.88	D2b	38.8	90.1	1.33	31.2	0.7
D3a	5/1/18 15:41	6.39	14.5	20	45	D3A	8.983	D3A	1.07	0.47	D3a	31.5	25.5	0.85	28.4	4.3
D3b	5/1/18 15:48	6.12	13.5	50	30	D3B	13.142	D3B	1.46	1.57	D3b	34.4	2.6	1.12	32.4	1.1
D4a	5/1/18 16:19	7.87	15.2	20	45	D4A	10.238	D4A	1.33	-0.25	D4a	29.4	25.1	0.41	21.6	0.5

Field Measurements						University of Nebraska					EPA R5 Laboratory					
Sample_ID	SampleDate_Time	pH_SU	Water_Temperature_C	Nitrate_Field_Test_mgl	Sample_Depth_from_Surface_ft	Sample_ID	NO3+NO2-N	Sample_ID	15N-NO3	18O-NO3	Sample ID	Chloride (mg/L)	Sulfate (mg/L)	Ammonia-N (mg/L)	Iron (ug/l)	Manganese (ug/l)
D4b	5/1/18 16:26	6.51	14	50	30	D4B	17.697	D4B	1.64	-1.72	D4b	63.7	93.0	2.82	75.8	3.5
D5a	5/2/18 6:38	8.5	10.7	2	45	D5A	0.451	D5A	-0.79	4.94	D5a	1.7	10.3	0.5	58.9	4.84
D5b	5/2/18 6:46	6.66	10	2	30	D5B	1.175	D5B	-8.93	-4.10	D5b	0.8	6.7	0.23	27.5	2.88
D6a	5/2/18 7:17	8.23	12.4	50	45	D6A	41.140	D6A	-0.83	-2.95	D6a	45.7	96.9	0.49	30.3	0.66
D6b	5/2/18 7:29	7.35	12	50	30	D6B	24.537	D6B	-2.70	-0.51	D6b	27.9	67.0	0.67	43.8	1.26
D7a	5/2/18 8:12	8.18	12.9	50	45	D7A	30.701	D7A	-2.62	1.53	D7a	46.8	68.7	U	6.14	2.28
D7b	5/2/18 8:19	6.56	13.8	50	30	D7B	32.208	D7B	-4.99	-3.17	D7b	41.2	112.0	0.49	41.1	6.69
D8a	5/2/18 8:55	8.3	13.3	50	45	D8A	48.759	D8A	8.24	4.86	D8a	50.6	88.8	0.77	22.3	3.24
D8b	5/2/18 9:11	6.9	13.6	50	30	D8B	39.010	D8B	0.23	2.27	D8b	66.2	86.4	0.68	44.1	9.73
D9a	5/2/18 9:45	8.16	13.8	20	45	D9A	30.252	D9A	-1.65	1.23	D9a	41.4	71.0	0.21	19.3	1.03
D9b	5/2/18 9:54	7.39	12.7	5	30	D9B	1.521	D9B	2.72	1.35	D9b	4.9	10.8	0.34	31.7	2.13
D10a	5/2/18 10:29	8.69	15.5	20	45	D10A	8.794	D10A	-6.75	-3.01	D10a	22.8	28.9	0.22	36.3	1.97
D10b	5/2/18 10:41	6.67	14	20	30	D10B	8.403	D10B	-1.72	0.08	D10b	21.6	31.6	0.31	29.1	5
D11a	5/2/18 11:19	7.04	14.3	20	45	D11A	28.038	D11A	1.96	5.26	D11a	22.5	21.4	U	3.33	2.58
D11b	5/2/18 11:42	6.08	13.5	20	30	D11B	14.492	D11B	-4.92	3.11	D11b	34.9	60.6	U	4.03	2.27
E1a	5/2/18 12:41	8.09	13.5	20	45	E1A	11.656	E1A	3.35	6.17	E1a	33.2	76.3	U	11.6	4.35
E1b	5/2/18 12:58	6.36	13.3	50	30	E1B	11.808	E1B	6.84	5.39	E1b	27.3	38.0	1.02	30.7	5.08
E2a	5/2/18 13:28	8.66	13.8	2	45	E2A	0.995	E2A	2.63	6.36	E2a	29.0	8.5	U	8.17	2.46
E2b	5/2/18 13:37	6.87	12.6	2	30	E2B	2.579	E2B	1.89	-0.20	E2b	1.8	13.0	0.73	29.9	3.93
E3a	5/2/18 14:03	8.56	14.3	5	45	E3A	3.831	E3A	-0.03	1.74	E3a	2.0	46.7	0.21	24.8	2.01
E3b	5/2/18 14:09	8.11	12.7	5	30	E3B	6.140	E3B	0.68	1.59	E3b	1.0	27.4	0.35	31.6	2.68
E4a	5/2/18 14:37	7.2	17.5	20	45	E4A	26.056	E4A	3.69	5.12	E4a	16.4	71.0	0.87	45.7	1.25
E4b	5/2/18 14:43	6.82	14.3	20	30	E4B	19.956	E4B	-0.84	4.71	E4b	33.7	62.8	1.37	49.3	5.97
E5a	5/2/18 15:08	8.06	14	50	45	E5A	28.326	E5A	1.29	4.91	E5a	30.8	69.3	0.22	26.7	1.31
E5b	5/2/18 15:13	6.9	13.7	20	30	E5B	17.491	E5B	2.59	5.44	E5b	28.9	61.3	0.73	44.6	2.77
E6a	5/2/18 15:38	8.62	13.4	0	45	E6A	0.149	E6A	-6.39	3.20	E6a	0.5	6.0	0.26	15.1	1.64
E6b	5/2/18 15:44	6.47	12.6	0	30	E6B	0.093	E6B	-2.48	4.47	E6b	0.7	5.6	0.39	42.9	1.62
E7a	5/2/18 16:09	5.98	14.2	20	45	E7A	16.130	E7A	3.76	7.91	E7a	33.0	41.1	U	19.5	2.11
E7b	5/2/18 16:35	5.73	13.2	50	30	E7B	13.811	E7B	-4.23	-2.39	E7b	32.4	47.5	U	10.9	1.52
E10a	5/3/18 7:15	7.06	10.3	2	45	E10A	0.427	E10A	-4.15	2.91	E8a	26.9	34.6	U	12.6	0.18

Field Measurements						University of Nebraska					EPA R5 Laboratory					
Sample_ID	SampleDate_Time	pH_SU	Water_Temperature_C	Nitrate_Field_Test_mgl	Sample_Depth_from_Surface_ft	Sample_ID	NO3+NO2-N	Sample_ID	15N-NO3	18O-NO3	Sample ID	Chloride (mg/L)	Sulfate (mg/L)	Ammonia-N (mg/L)	Iron (ug/l)	Manganese (ug/l)
E10b	5/3/18 7:27	7.05	10	0	30	E10B	0.042	E10B	12.57	35.93	E8b	37.1	60.6	0.46	33.9	0.56
E8a	5/3/18 8:40	5.76	11.3	20	45	E8A	28.579	E8A	11.47	15.97	E10a	0.6	8.5	U	7.83	0.24
E8b	5/3/18 8:48	6.18	10.9	50	30	E8B	21.058	E8B	6.01	9.17	E10b	1.1	10.2	U	44.4	1.01
E9a	5/3/18 9:53	6.75	11	10	45	E9A	20.791	E9A	29.64	22.79	E9a	31.2	64.8	U	15.9	0.24
E9b	5/3/18 10:02	6.15	10.9	20	30	E9B	20.229	E9B	9.39	13.17	E9b	32.1	62.3	0.34	40.5	1.04